Russian Chemical Reviews **73** (5) 455 – 486 (2004) © 2004 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2004v073n05ABEH000891

Chemical crystallography of fullerenes

I S Neretin, Yu L Slovokhotov

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Abstract. The state-of-the-art in the structural investigations into fullerene derivatives is surveyed. The crystal structures of individual fullerenes and of their derivatives determined experimentally by single-crystal X-ray diffraction are systematised. The results of powder X-ray diffraction and EXAFS spectroscopy are overviewed for those classes of derivatives that have been insufficiently studied by single-crystal X-ray diffraction. Patterns of packing of the fullerene spheres encountered in crystal structures are described and representative examples of the most typical motifs are given. Reasons for the rotational disorder, which often hampers structure determination for fullerene derivatives, and its classification are considered. A model of the 'rubber cavity' is introduced, which allows prediction of typical mutual orientations of disordered molecules. The redistribution of bond lengths upon σ- and π-functionalisation of the carbon core is analysed based on the information retrieved from the Cambridge Structural Database. Factors affecting the molecular packing density in crystalline derivatives of fullerenes are discussed in relation to the quality of the diffraction data attainable for them. The bibliography includes 282 references.

I. Introduction

Fullerenes are a family of allotropic forms of carbon, the crystals of which are built up of hollow spheroidal molecules C_n united by van der Waals interactions. The C_{60} (also referred to as buckminsterfullerene) and C_{70} fullerenes and their derivatives are the most studied. To date, the C_n fullerenes, where $n = 60, 70, 76, 78, 80, 82, 84, 88$, and 92 (see Ref. 1) have been isolated as individual substances.

I S Neretin, Yu L Slovokhotov A N Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 119991 Moscow, Russian Federation. Fax (7-095) 135 50 85. Tel. (7-095) 135 93 04. E-mail: ivan@neretin.ru (I S Neretin), slov@ineos.ac.ru (Yu L Slovokhotov)

Received 15 December 2003
Uspekhi Khimii **73** (5) 492 – 525 (2004); translated by Ya V Zubavichus

The overall number of publications on fullerenes by the end of 2001 exceeded 10 000, however, the fraction of those devoted to single-crystal X-ray diffraction studies remains relatively small (*i.e.*, < 400 structures by the end of 2003). A large concentration of defects and twinning are very common for single crystals of fullerenes and their derivatives. Furthermore, the quasi-spherical C_n molecules were found to be rotationally disordered in the crystal structures of many fullerene derivatives. The co-existence of different orientations of a fullerene molecule similar in energies in one crystal results in a deterioration of the experimental diffraction pattern. The problem of the rotational disorder is of special importance in the van der Waals complexes comprising chemically non-modified fullerene molecules. On the other hand, co-crystallisation of different difficult-to-separate addition isomers becomes a serious issue for the chemically modified fullerenes. For higher fullerenes, the overall structural disorder may be increased due to the presence of different geometrical isomers statistically occupying equivalent crystallographic positions of the crystal lattice. All these factors hamper diffraction studies and decrease the accuracy of structure elucidation. However, it is these methods and, primarily, single-crystal X-ray diffraction, that are the most important in the studies of fullerene derivatives because of their structural complexity.

Several reviews on the crystal structures of particular groups of fullerene derivatives have been published,[2–6] but the general regularities of molecular and crystal structures within the whole class of compounds are still lacking. In the present review, the results of single-crystal X-ray diffraction studies of fullerene derivatives are surveyed and distinctive features of their structures are analysed. Special attention is paid to the crystallographic data retrieved from the Cambridge Structural Database (CSD) and original journal papers. The available information still admits a comprehensive coverage within one review paper, thus making it possible to reveal the most general tendencies in the crystallography of fullerene derivatives. For certain compounds closely related to the subject of the present review, the results of other experimental techniques (such as gas electron diffraction, neutron diffraction, powder X-ray diffraction, and XAFS spectroscopy) are also considered.

II. The molecular structures of fullerenes

The stability of a C_{60} molecule having the symmetry of a truncated icosahedron was predicted in the early 1970s independently by Osawa [7] and by Bochvar and Gal'pern.[8] Experimentally, C_{60} has been registered for the first time as a molecular ion in a mass-spectral analysis of gaseous species produced by laser ablation of graphite.[9] The nonequilibrium cooling of carbon vapour gives rise to formation of various C_n clusters with C_{60} being the dominant. Clusters with even smaller n have been detected in mass spectra of graphite sublimation products, however, the respective individual substances have not been isolated so far.

Later, a method for production of fullerenes in macroscopic quantities has been elaborated based on graphite evaporation in an electrical arc plasma with graphite electrodes performed in an inert atmosphere (He or Ar at a pressure of 10–100 mbar).[10] The soot produced in this process contains up to 15%–20% of fullerenes that are further extracted and separated by column chromatography. C_{60} (85%) and C_{70} (14%) are the dominant products while the remaining 1% falls within higher fullerenes, such as C_{76}, C_{84}, C_{90}, and so on.

The molecules of fullerenes represent convex polyhedra with carbon atoms in their vertices, which have only penta- and hexagonal faces, *i.e.*, the carbocycles characterised by the minimum steric strain. According to the Euler theorem, such polyhedra have exactly twelve pentagonal and any number of hexagonal faces.† The simplest fullerene-like polyhedron is a pentagondodecahedron, which has no hexagonal faces. The respective saturated hydrocarbon (*i.e.*, dodecahedrane $C_{20}H_{20}$) was prepared in the 1980s by a complex multistage organic synthesis.[11] Non-modified fullerene C_{20} is, most likely, unstable due to the large steric strain in the unsaturated carbon core. Nevertheless, C_{20} clusters have been detected in the gas phase upon thermal decomposition of brominated dodecahedrane.[12] The isolation of the C_{36} fullerene has been reported [13] but its crystal structure has not been determined. Probably, this structure involves C_{36} units covalently bound to each other rather than independent molecules.

Virtually all fullerenes, for which molecular structures have been determined experimentally, obey the so called Isolated Pentagon Rule, or IPR:[14] the pentagonal rings in their molecules must not have shared vertices. Taking this rule as a requisite, the simplest fullerene is buckminsterfullerene C_{60} (Fig. 1 *a*) and the next one is C_{70}. Furthermore, any fullerenes with even numbers of carbon atoms are allowed. The isolated pentagon rule substantially reduces the number of allowed fullerene structures. For instance, theoretically, the IPR-forbidden C_{66} cluster will have 4478 geometrical isomers if this rule is not taken into account.[15] Note, however, that metallofullerenes such as $Sc_2@C_{66}$ and $Sc_3N@C_{68}$ (see Refs 15, 16) have been isolated. Apparently, this means that the IPR is not stringent and may be violated, at least, in the case of chemically modified carbon cages.

For every fullerene starting from C_{76}, there are several geometrical isomers complying with the IPR. Some of them are chiral and may occur as enantiomers. The number of the fullerene-type polyhedra (M) complying with the IPR as a function of the number of atoms in the carbon cage (n) is given below:

n	60	62–68	70	72	74	76	78	80	82	84	86	90	96
M	1	–	1	1	1	2	5	7	9	24	35	46	187

A topological nomenclature of fullerenes taking into account their probable chirality has been suggested.[17] The relative stabilities of different fullerenes have been thoroughly studied theoretically by methods of quantum chemistry.[18, 19] In particular, the calculations predicted instability of C_{72} and C_{74} fullerenes (complying with the IPR) as neutral molecules.[20] These 'quantum chemistry-forbidden' fullerenes should be highly reactive biradicals. However, they can be stabilised as dianions, in particular, in endohedral derivatives, in which such a stabilisation is achieved owing to charge transfer from the metal atom located inside the carbon cage.[21]

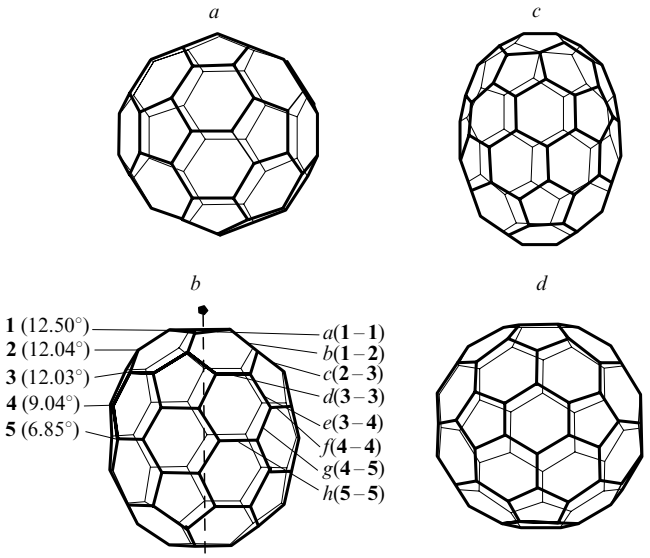


Figure 1. Molecular structures of C_{60} (*a*), C_{70} (*b*), C_{76} (*c*) and I_h isomer of C_{80} (*d*);
(*b*) (to the left): types of symmetrically nonequivalent carbon atoms and their spherical excesses; (to the right): types of bonds and atoms forming these bonds.

The molecular structures of best studied carbon cores are shown in Fig. 1. Buckminsterfullerene C_{60} having the icosahedral symmetry (I_h) is the most abundant fullerene. Its molecular structure has been first established based on the ^{13}C NMR data (the spectrum comprises only one singlet).[22] All carbon atoms in the C_{60} molecule are symmetrically equivalent (*i.e.*, they are transferred to each other by symmetry operation describing the molecule). Meanwhile, there are two nonequivalent types of bonds: those joining pentagons and hexagons and those joining two hexagons (referred to as 5/6 and 6/6 bonds, respectively). The latter bond is characterised by a larger π-contribution and thus is shorter. The CC distances in C_{60} are 1.40 Å (6/6) and 1.46 Å (5/6) according to the gas electron diffraction data.[23] The corresponding mean values for 52 ordered molecular complexes of C_{60} calculated by us based on the crystallographic data retrieved from the CSD are 1.39 Å (6/6) and 1.45 Å (5/6). The bond angles are 108° in pentagons and 120° in hexagons. The spherical excess φ, defined as a difference between 360° and the sum of the bond angles at a certain carbon atom, is, in the case of C_{60}, 12° for all carbon atoms.

After C_{60}, the non-centrosymmetrical C_{70} (see Fig. 1 *b*) having the D_{5h} symmetry is the next most studied fullerene. It differs from C_{60} by an additional equatorial belt of hexagons. In C_{70}, there are 5 symmetrically nonequivalent carbon atoms and 8 different bond types, which is consistent with the NMR data.[24] For the free molecule, the bond lengths have been determined using gas electron diffraction [25] coupled with the quantum chemistry optimisation of the molecular geometry within the density functional theory. The bond lengths in C_{70} from the electron diffraction data and from the single-crystal X-ray diffraction data for the molecular complex $C_{70} \cdot 6S_8$, which has been determined with the highest accuracy,[26] are listed in Table. 1. In C_{70}, the longest bond is the equatorial bond *h* (type 6/6) (see Fig. 1 *b*). All

† The Euler theorem states that for any convex polyhedron, $V - E + F = 2$, where V, E and F are the numbers of vertices, edges and faces of the polyhedron, respectively. Let a polyhedron be composed of n pentagonal and m hexagonal faces. Then, $F = n + m$, $E = (5n + 6m)/2$, since each edge is shared by two faces and $V = (5n + 6m)/3$, since each vertex resides in the intersection of three edges. After substitution of F, E and V in the above equation and simplification thereof, one gets $n = 12$.

Table 1. Bond lengths in the molecule of fullerene C_{70} (for notations, see Fig. 1 *b*).

Bond	Type	Number of bonds	Length (Å) determined using	
			gas electron diffraction [25]	single-crystal X-ray diffraction [26]
a	5/6	10	1.46	1.45
b	6/6	10	1.39	1.38
c	5/6	20	1.45	1.45
d	6/6	10	1.39	1.37
e	5/6	20	1.47	1.45
f	5/6	10	1.42	1.43
g	6/6	20	1.40	1.41
h	6/6	5	1.54	1.47

other 5/6 and 6/6 bonds are similar in length and character to the respective bonds in C_{60}. The spherical excess is the largest for the carbon atoms located at the pole positions of the molecule and the smallest for the equatorial atoms.

The molecular structures of higher fullerenes are less studied. The C_{76} fullerene, which has been isolated as a pure substance, represents a chiral isomer with D_2 symmetry (see Fig. 1 *c*) according to the single-crystal X-ray diffraction data of its molecular complex with sulfur $C_{76} \cdot 6\,S_8$.[27] The crystal contained a racemic mixture of enantiomers statistically occupying the same crystallographic positions.

The C_{78} fullerene is a mixture of two isomers with C_{2v} and D_3 symmetry in a ratio of 5 : 1, according to the NMR data.[28] The dominant isomer of the C_{80} fullerene has D_{2d} symmetry,[29] though an isomer with D_{5h} symmetry has also been isolated.[30] An isomer of C_{80} with icosahedral symmetry I_h (see Fig. 1 *d*), which is the least stable in the free form according to the quantum chemistry calculations, has been prepared and structurally characterised as an endohedral derivative. In these substances, the carbon cage is stabilised due to a charge transfer from the metal atoms to the carbon core. In contrast to C_{60}, which possesses regularly alternating 6/6 and 5/6 bonds in each hexagon, this I_h isomer of C_{80} comprises perylene fragments with five fused hexagons.

The structural study of higher C_{76} and C_{82} fullerenes as solvates with toluene using synchrotron radiation (SR) powder X-ray diffraction [31] has been conducted but not yielded reliable geometry of their carbon cores.

According to the quantum chemistry calculations,[19] the relative stabilities of isomeric fullerene cages C_n^{q-} change depending on the charge q (Fig. 2). The results of single-crystal X-ray diffraction studies of the endohedral derivatives $M_n@C_{82}$ and $M_n@C_{84}$ are discussed below (Section X).

According to the IR data,[32] pure C_{84} fullerene represents a mixture of two major isomers with D_{2d} and D_2 symmetry. Its π-complex with iridium, which has been isolated and structurally characterised,[33] contains a carbon cage having D_{2d} symmetry with a contribution of other unidentified isomers. The NMR data on the C_{88} fullerene have been interpreted [34] as a superposition of spectra attributable to three isomers. This spectral assignment has been made on the basis of the quantum chemistry calculations of all possible isomers complying with the IPR.

Among even larger fullerenes, C_{92} has been isolated and partially separated into fractions. One of them contained the only isomer with C_{2v} symmetry (according to the ^{13}C NMR data), whilst the other fraction represented a mixture of isomers.[35] Furthermore, there has been a report on a preparation of an individual cluster-'onion' (not studied structurally) with a C_{60} internal core and a C_{240} outer shell.[36]

Upon partial substitution of boron or nitrogen atoms for the carbon atoms, various heterofullerenes are produced. One of them with the stoichiometry $C_{59}N$ has been isolated and studied by means of powder X-ray diffraction using Rietveld refinement. This substance was identified as a molecular crystal containing dimeric molecules $(C_{59}N)_2$.[37] A cationic derivative of this heterofullerene, $[(C_{59}N^+CB_{11}H_6Cl_6)_2Ag] \cdot 3(o\text{-}C_6H_4Cl_2)$, has been studied by single-crystal X-ray diffraction.[38] In the crystal structure of this compound, the nitrogen atom is disordered over two positions in the $C_{59}N^+$ cluster, which is isolectronic and isostructural to buckminsterfullerene.

The energy diagram of the molecular π-orbitals for C_{60} has been calculated for the first time by the simple Hückel method.[8] The energy level diagrams for C_{60} and C_{70} are shown in Fig. 3. Due to the high symmetry of the buckminsterfullerene molecule, its lowest unoccupied molecular orbital (LUMO) is triply degenerate and its highest occupied orbital (HOMO) is quintuply

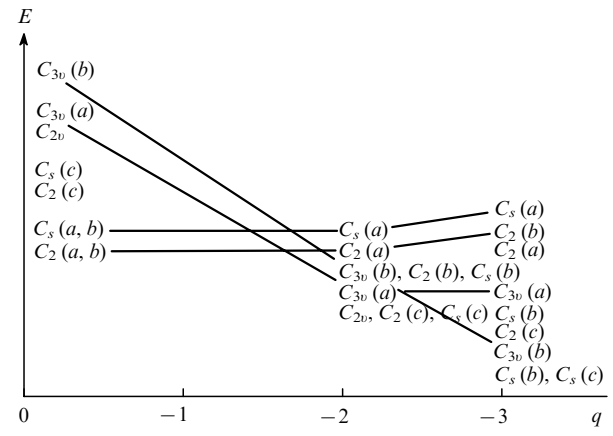


Figure 2. The relative stabilities of different geometrical isomers of C_{82}^{q-} (see Ref. 19).

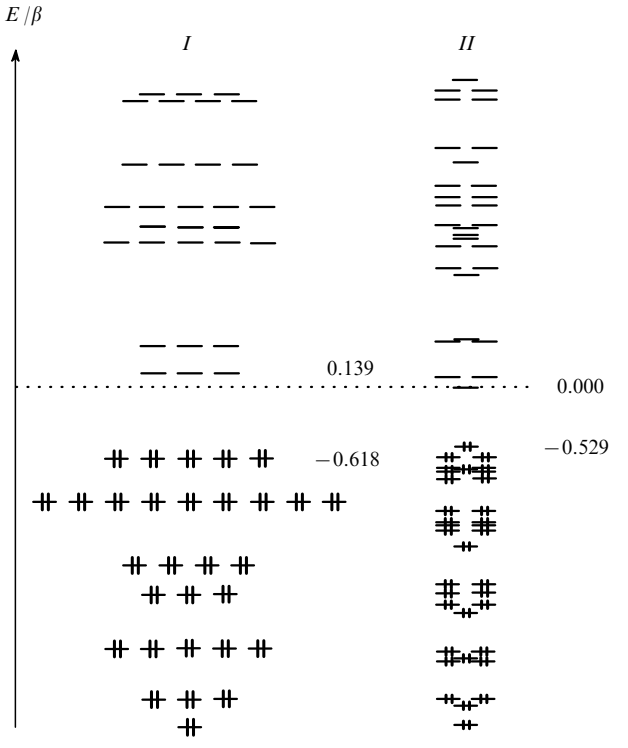


Figure 3. The energy diagram of π-orbitals in C_{60} (*I*) and C_{70} (*II*) in units of the resonance integral (β). The dotted line corresponds to the energy of 2p-AOs of an isolated carbon atom.

degenerate (see Fig. 3 *I*). The less symmetrical C_{70} molecule has only nondegenerate and doubly degenerate levels (see Fig. 3 *II*). On average, the energy difference (LUMO – HOMO) in stable C_n fullerenes, as determined by the quantum chemistry calculations, decreases with an increase in n approaching ultimately zero (as in graphite [39]).

Thus, polyhedral molecules of fullerenes retain important features of planar π-conjugated systems, such as low-energy π-bonding and stabilisation of alternant structures. As a result, energies of their frontier orbitals can be fairly reproduced using the simple Hückel method. Meanwhile, the C_n molecules themselves manifest many properties of unsaturated hydrocarbons, *e.g.*, addition reactions to 'double' 6/6 bonds and π-complexation to metals are typical of them. On the other hand, non-modified fullerenes do not contain fully delocalised π-systems, similar to those in aromatics, and their double bonds remain partially localised.

III. Crystal structures of individual fullerenes

The fullerene-containing substances, crystal structures of which have been deposited into CSD (2003 version) are listed in Table 2. The overall number of related CSD entries is 382 (including repeated studies). In several cases, no coordinates of carbon atoms have been deposited into the CSD. All the compounds are subdivided into classes according to the extent of the chemical modification of the corresponding fullerene molecule. Table 2 also contains single-crystal X-ray diffraction results published in scientific journals but not included in the CSD version of October, 2003, as well as some substances studied by powder X-ray diffraction.

Pure crystalline buckmisterfullerene C_{60} prepared by resublimation *in vacuo* possesses a face-centred cubic (fcc) lattice.[53] At room temperature, the fullerene molecules in this structure are rotationally disordered. Upon a decrease in the temperature down to 258 K, a phase transition occurs, which is accompanied by partial ordering of the molecules and lowering of the symmetry of the cubic lattice from $Fm3m$ to $Pa\bar{3}$. Upon further cooling, the dynamic disorder is gradually replaced by the static disorder.[54] At even lower temperatures (*e.g.*, at 5 K),[55] the crystal reveals a statistical mixture of only two molecular orientations (neutron diffraction data), however, no complete 'freezing' of this degree of freedom has been reached. The shortest interatomic C···C contacts between the neighbouring C_{60} molecules (3.00 Å) are almost 0.2 Å shorter than the interlayer C···C distances in graphite,[56] *i.e.*, they are likely to correspond to the van der Waals repulsion compensated by the mutual attraction of more distant atoms from the neighbouring molecules. Most probably, no local charge transfer within the carbon cage is involved, which would have given rise to the electrostatic attraction of the neighbouring molecules mutually oriented so as to expose oppositely charged sides (initially proposed as an explanation for the shortened C···C distances, see Ref. 57). Physical investigations into the dynamics of the disordered fullerene clusters in crystals will not be addressed in any detail here since this review is focused primarily on the structures of fullerene derivatives in their relation to chemical properties.

Under special conditions, it is possible to prepare polycrystalline powder of the metastable hexagonal modification of C_{60} in which the fullerene molecules make up a two-layer close packing of spheres.[58, 59] Earlier reports [60] on another hexagonal modification of buckminsterfullerene with the parameters $a = 33.54$ Å and $c = 10.11$ Å have not been confirmed. Probably, these parameters correspond to a fullerene-rich solvate rather than pure fullerene.

The C_{70} fullerene composed of molecules that may be approximated as ellipsoids has a more complex phase diagram. The high-temperature fcc phase, which is characterised by isotropic rotations of the molecules, converts, upon a decrease in the temperature down to 340 K, into a trigonal (rhombohedral) phase, in which the long axes of the ellipsoids are oriented along the crystallographic three-fold axis, and the rotational disorder appears only due to revolution around them (Fig. 4). At even lower temperature (*viz.*, 280 K), the molecules get completely ordered forming a monoclinic phase similar to the trigonal one as regards the lattice parameters ($a \approx c$, $\beta \approx 120$). As for C_{60}, a metastable modification of C_{70} with the hexagonal close packing (hcp) of isotropically disordered molecules is known. Upon a decrease in the temperature, this phase undergoes two phase transitions accompanied by an ordering of the molecular rotations, analogous to those described above. Apart from the two regular high-temperature modifications, *viz.*, fcc and hcp, there exists a series of intermediate phases characterised by irregular layer sequences.[61]

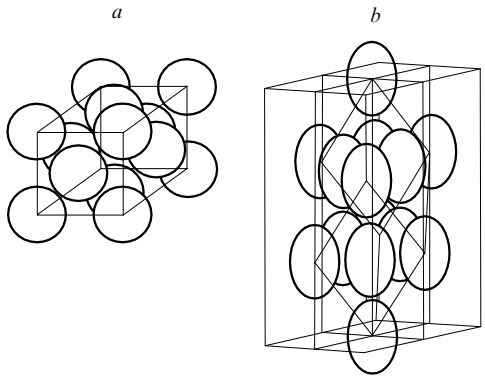


Figure 4. Schematic representation of the crystal structure of the fcc phase of C_{60} (*a*) and rhombohedral phase of C_{70} (*b*).

For some of the higher fullerenes with rather spheroidal molecules, only high-temperature fcc phases have been detected, while information on the phase transitions at low temperatures is lacking.[62] For the C_{84} fullerene, two phase transitions at 235 K and 181 K have been revealed by powder X-ray diffraction, although the structures of the low-temperature phases have not been determined.[63]

IV. Molecular complexes

Numerous derivatives of fullerenes may be classified as molecular complexes with non-polar molecules. Sometimes, they are also referred to as mixed or van der Waals crystals. As was first pointed out by A I Kitaygorodsky,[64] the most energetically favourable molecular packing in a crystal formed exclusively by van der Waals interactions normally coincides with the densest one. Any close packing of large spheroidal C_n molecules contains cavities of an appreciably large size. Therefore, fullerenes readily form molecular complexes (clathrates, inclusion compounds) with many 'guest' molecules. The structures and properties of such substances have been reviewed by several authors.[2, 3, 6] Many crystallographic regulations observed for this class of compounds may be extended to include fullerene derivatives.

The cavities in the parent close packing of fullerene 'spheres' can accomodate only single atoms, for instance, of alkali metals (see Section V). The majority of crystalline fullerene molecular complexes contain looser structural motifs of the C_n clusters formed as a result of incorporation of larger molecules or ions. It is convenient to characterise these motifs with the 'partial' molecular coordination number (MCN), which is the number of neighbouring fullerene clusters forming the van der Waals C···C contacts in the range 3.2 – 3.5 Å with the central cluster. For

Table 2. Structurally characterised fullerene derivatives (only one mention of each structure is given, repeated and independent studies are omitted).

CSD Refcode or (Ref.)	Formula [a]	*R*-factor	Motif	MCN (see [b])	*T*/K
SOCTOT01	C_{60}	0.100	fcc	12	110
SOCTOT02	C_{60}	0.059	"	12	295
QUQDOV	$(C_{70})_\infty$	0.066	distorted hcp	12	100
Solvates and molecular complexes					
MAPSUR	$C_{60} \cdot 1.5\,CS_2$	0.058	3*D* framework	10	90
POFKUQ	$C_{60} \cdot n\text{-}C_5H_{12}$	0.130	"	10	295
EDEWAL	$C_{60} \cdot C_2H_3Cl_3$	–	–	–	223
TEYCEF	$C_{60} \cdot 2\,(m\text{-}C_6H_4Me_2)$	0.147	3*D* framework	10	20
PIGWUX	$C_{60} \cdot 2\,CCl_4$	–	simple hexagonal	8	295
YOLTEY	$C_{60} \cdot 2\,CHBr_3$	–	the same	8	295
YOLTIC	$C_{60} \cdot 2\,CHCl_3$	–	"	8	295
YOLTOI	$C_{60} \cdot 2\,CH_2Cl_2$	–	–	–	295
HOSJAA	$C_{60} \cdot 2\,PhBr$	0.057	hexagonal layers	6	150
JUGCET	$C_{60} \cdot 4\,C_6H_6$	0.101	honeycomb	6	173
YOLTAU	$C_{60} \cdot 13\,CCl_4$	–	isolated	0	295
YOLSOH	$C_{60} \cdot 13\,C_6H_{12}$	–	"	0	295
JOCSOJ	$(C_{60}, C_{70}) \cdot x\,C_6H_{12}$	0.109	"	0	295
YOLSUN	$C_{70} \cdot 13\,C_6H_{12}$	–	"	0	295
NUDDOF	$C_{70} \cdot m\text{-}C_6H_4Me_2$	0.213	3*D* framework	10	295
ZOYSOV	$C_{76} \cdot PhMe$	0.048	simple hexagonal	8	295
ZOYSEL	$C_{82} \cdot PhMe$	–	the same	8	295
XIFMEE	$C_{60} \cdot 3\,TiCl_4$	0.038	diamond-like	4	180
XOBVIT	$C_{70} \cdot 2\,TiCl_4$	0.059	3*D* framework	7, 8	180
JUVYAA	$C_{60} \cdot CH_2I_2 \cdot C_6H_6$	0.055	simple hexagonal	8	122
LAVNIF	$C_{60} \cdot I_2 \cdot PhMe$	0.076	3*D* framework	8	143
MAQFIT	$4\,C_{60} \cdot 3\,TDZ$	0.046	"	9	100
YITCUZ	$C_{60} \cdot S_8 \cdot CS_2$	0.069	honeycomb	8	295
HEGPAK	$C_{60} \cdot 2\,S_8$	0.041	diamond-like	4	295
TONDUV	$C_{60} \cdot TMPD$	0.080	hexagonal layers	6	295
SOMGIK	$C_{60} \cdot 3\,[p\text{-}C_6H_4(OH)_2]$	0.198	simple cubic	6	295
MIMROP	$C_{60} \cdot PBMP$	0.131	3*D* framework	6	293
NIYBOM	$2\,C_{60} \cdot TPBP \cdot 4\,CS_2$	0.049	"	5	170
NIRLOP	$C_{60} \cdot Ph_3SiH$	0.156	honeycomb	6	213
YEKBOF	$3\,C_{60} \cdot 2\,CTV \cdot PhMe$	0.142	hexagonal layers	6	295
CEMPAL	$C_{60} \cdot AT$	0.086	honeycomb	6	150
ZUMCIT	$C_{60} \cdot BTX \cdot CS_2$	0.057	columns	2	295
TAWKEH	$C_{60} \cdot CCTV$	0.123	chains	2	183
PASQAB	$C_{60} \cdot DAN \cdot 3\,C_6H_6$	0.069	tetragonal layers	4	295
CEMNUD	$C_{60} \cdot 2\,Trip \cdot 2\,(o\text{-}C_6H_4Me_2)$	0.095	hexagonal layers	6	150
FOFKEQ	$C_{60} \cdot OPCTSil \cdot 0.5\,PhMe$	0.051	double chains	4	123
YOLVOK	$C_{60} \cdot 2\,HMTPH$	0.098	–	–	295
BACQAX	$C_{60} \cdot TBBCN \cdot 1.5\,PhMe$	0.114	columns	2	153
KUVNOE	$C_{60} \cdot 2\,Cp_2Fe$	0.060	hexagonal layers	6	143
NAGNAK	$C_{60} \cdot 3\,C_6H_6 \cdot 2\,Pd_6Cl_{12}$	0.093	chains	2	130
PIGPEA	$C_{60} \cdot Cp_4Fe_4(CO)_4 \cdot 3\,C_6H_6$	0.065	–	–	173
NUWYOT	$2\,C_{60} \cdot 4\,BEDT\text{-}TTF \cdot Cp_2Fe \cdot 0.5\,CS_2$	–	–	–	295
SADVUO	$C_{60} \cdot TBrCalix[3]$	0.105	diamond-like	4	295
SADWAV	$C_{60} \cdot TBuCalix[3]$	0.198	graphite-like	3	295
NIFYAC	$C_{60} \cdot TMCalix[5] \cdot 4\,H_2O$	0.085	island	1	295
NIFXUV	$C_{60} \cdot PMCalix[5] \cdot CH_3OH \cdot 3\,H_2O$	0.097	"	1	295
FAJFAX	$C_{60} \cdot TBTPCalix[4]$	0.117	columns	2	173
NOBLEV	$2\,C_{60} \cdot Calix[6] \cdot PhMe$	0.119	3*D* framework	5	173
PUJROB	$C_{60} \cdot TPCalix[4]R \cdot 4\,Pr^iOH \cdot o\text{-}C_6H_4Cl_2$	0.119	isolated	0	173
TUDCOK	$C_{60} \cdot 2\,DIDMCalix[5] \cdot 8\,H_2O$	0.168	"	0	295
JAYDIW	$C_{60} \cdot 2\,TBzCalix[3]$	0.136	"	0	273
BOXQOU	$C_{60} \cdot 2\,TBuCalix[3]N$	0.154	"	0	193
NIGPOI	$C_{60} \cdot 2\,TITBCalix[4]$	0.089	"	0	295
JAXYIQ	$C_{60} \cdot 2\,PBzCalix[5] \cdot 2\,PhMe$	0.124	"	0	173
ADACIR	$5\,C_{60} \cdot 4\,Calix[5] \cdot 2\,PhMe$	0.209	complex chains	4, 6	173
MEQGIY	$C_{60} \cdot biCalix[5] \cdot 2\,PhMe$	0.098	isolated	0	148
FIBVIV	$C_{60} \cdot TMTSeF \cdot 0.5\,C_6H_6$	0.061	3*D* framework	6	295
NIXPOZ	$C_{60} \cdot TMTSeF \cdot 2\,CS_2$	0.047	tetragonal layers	4	295
UCIKEW	$C_{60} \cdot DBTTF \cdot C_6H_6$	0.069	–	–	153
XOCJII	$C_{60} \cdot MDT\text{-}TTF \cdot 2\,CS_2$	0.070	hexagonal layers	6	293

Table 2 (continued).

CSD Refcode or (Ref.)	Formula [a]	*R*-factor	Motif	MCN (see [b])	*T*/K
Solvates and molecular complexes					
YOCFOL	$C_{60}\cdot$ BDMT-TTeF$\cdot CS_2$	0.038	–	–	295
LITPUZ	$C_{60}\cdot$ DTDSeF	0.050	tetragonal layers	4	295
FONPED	$C_{60}\cdot 1.33\,S_4N_4\cdot 0.67\,C_6H_6$	0.132	–	–	153
SUGBUR	$C_{60}\cdot$ BEDTB(EDT)$\cdot CS_2$	0.073	double chains	3	295
KUMMEK	$C_{60}\cdot 2$ BEDT-TTF	0.058	the same	4	150
TODZUH	$C_{60}\cdot 2$ DMTEDT-TTF	–	–	–	295
TOFBAR	$C_{60}\cdot 2$ TMTTF	–	–	–	295
DAGSUZ	$C_{60}\cdot 2$ TMDTDM-TTF$\cdot 3\,CS_2$	0.060	–	–	153
UBOJOK	$2\,C_{60}\cdot H_2TPP\cdot 4\,C_6H_6$	0.062	puckered graphite	3	120
UBOJUQ	$2\,C_{60}\cdot H_2TPP\cdot 3\,C_6H_6$	0.131	3*D* with channels	5	120
VEMNOQ	$C_{60}\cdot H_2TPP\cdot 3$ PhMe	0.087	chains	2	203
VEMQAF	$3\,C_{60}\cdot 2$ TDMPP$\cdot 4$ PhMe	0.092	isolated	0	203
VEMQEJ	$C_{60}\cdot$ TPivP	0.088	"	0	295
VEMPEI	$C_{60}\cdot H_2$TDBPP	0.091	"	0	203
ZAPNEJ	$C_{60}\cdot 2\,H_2$-ODAPz$\cdot$ PhMe	0.165	columns	2	295
BAQRUG	$C_{60}\cdot$ CuTMCTD	0.104	puckered layers	5	123
PIQHOM	$C_{60}\cdot$ NiTMCTD	0.052	the same	5	173
HIVKEC	$C_{60}\cdot$ NiOMCTD$\cdot 2\,CS_2$	0.088	chains	2	123
FOPZEP	$C_{60}\cdot$ NiODAPz	0.061	"	2	295
CELYOH	$C_{60}\cdot$ ClFeOEP$\cdot CHCl_3$	0.126	"	2	130
ABOSOZ	$C_{60}\cdot$ AgOEP$\cdot 2\,C_6H_6$	0.036	puckered graphite	3	83
QARPUU	$C_{60}\cdot$ PdOEP$\cdot 1.5\,C_6H_6$	0.079	graphite-like	3	83
QARQAB	$C_{60}\cdot$ CuOEP$\cdot 2\,C_6H_6$	0.037	"	3	83
QARQEF	$C_{60}\cdot$ Ru(CO)OEP$\cdot 2$ PhMe	0.095	chains	2	83
KEQKIA	$C_{60}\cdot 2\,Ph_3AsAuCl$	0.032	isolated	0	140
LOHSOQ	$C_{60}\cdot 2\,Ph_3PAuCl$	0.078	"	0	295
QUFLUY	$2\,C_{60}\cdot$ CoTAP$\cdot 3.3\,(o\text{-}C_6H_4Cl_2)\cdot 0.45\,C_6H_6$	0.083	island	1	146
FOPYEO	$C_{60}\cdot 2$ CuODAPz$\cdot 2\,C_6H_6$	0.054	isolated	0	295
CELTIW	$C_{60}\cdot 2$ CoOEP$\cdot CHCl_3$	0.082	"	0	154
CELVAQ	$C_{60}\cdot 2$ ZnOEP$\cdot CHCl_3$	0.069	"	0	156
CELVUK	$C_{60}O\cdot 2$ CoOEP$\cdot CHCl_3$	0.069	"	0	130
QARQIJ	$C_{60}\cdot 2$ ZnOEP$\cdot 2\,C_6H_6$	0.167	"	0	83
ABOSUF	$C_{60}\cdot 2$ NiOEP$\cdot 2$ PhCl	0.077	"	0	83
TIKHAW	$C_{60}\cdot$ CoTDBPP	0.032	"	0	83
UBOJIE	$C_{60}\cdot 2$ CuTPP	0.058	columns	2	110
XEYZAC	$C_{60}\cdot$ BPZnOEP	0.075	isolated	0	163
YIKVET	$C_{60}\cdot 6\,Ph_3Sb$	0.041	"	0	130
BEJLOR	$C_{70}\cdot 2\,Cp_2Fe$	0.077	hexagonal layers	7	130
NOBLIZ	$2\,C_{70}\cdot$ Calix[6]$\cdot$ PhMe	0.126	the same	7	173
DATQEU	$C_{70}\cdot$ BTX$\cdot 0.5\,CS_2$	0.080	tetragonal layers	4	295
HAZQAA	$C_{70}\cdot$ OMDBCTD	0.047	puckered layers	5	173
VEMQUZ	$2\,C_{70}\cdot$ NiTTolP$\cdot 2$ PhMe	0.071	double chains	3	198
HASWIH	$2\,C_{70}\cdot 9\,[p\text{-}C_6H_4(OH)_2]\cdot 2\,C_6H_6$	0.104	island	1	295
WITRAS	$3\,C_{70}\cdot 4$ BNDTY$\cdot 4\,C_6H_6$	0.090	distorted simple cubic	4	295
GOSYOC	$C_{70}\cdot C_2B_{10}H_{12}\cdot$ CTV$\cdot C_6H_4Cl_2$	0.094	chains	2	123
CELWAR	$C_{70}\cdot$ CoOEP$\cdot CHCl_3\cdot C_6H_6$	0.102	"	2	156
CELYEX	$C_{70}\cdot$ NiOEP$\cdot CHCl_3\cdot C_6H_6$	0.099	"	2	130
CELYIB	$C_{70}\cdot$ CuOEP$\cdot CHCl_3\cdot C_6H_6$	0.126	"	2	156
QEZFIK	$C_{60}\cdot$ PdBPPyP$\cdot 2\,C_6H_{14}\cdot 0.5$ PhMe	0.075	island	1	213
LAZMEE	$C_{70}\cdot 6\,S_8$	0.037	hexagonal layers	6	100
UBOJEA	$C_{70}\cdot$ CuTPP$\cdot 1.5$ PhMe$\cdot 0.5\,C_2HCl_3$	0.103	chains	2	110
VEMQOT	$C_{70}\cdot$ ZnTPP	0.102	"	2	203
VEMQIN	$C_{70}\cdot H_2$TDMPP$\cdot 4$ PhMe	0.143	isolated	0	295
RATCUK	$C_{76}\cdot 6\,S_8$	0.040	hexagonal layers	6	180
(40)	$C_{60}\cdot CHBr_3$	0.137	3*D* framework	10	150
(41)	$C_{60}\cdot 2$ PhI	0.030	hexagonal layers	6	110
(41)	$C_{60}\cdot 2\,(m\text{-}C_6H_4Br_2)$	0.029	cubic framework	6	110
(41)	$C_{60}\cdot 3\,(o\text{-}C_6H_4Br_2)$	0.144	diamond-like	4	110
(42)	$C_{60}\cdot 1,3,5\text{-}C_6H_3Ph_3$	0.078	graphite-like	3	110
(42)	$C_{60}\cdot 2\,(1,3,5\text{-}C_6H_3Ph_3)\cdot$ PhCl	0.090	columns	2	110
(43)	C_{60}^{-}TDAE$^{+}\cdot 2$ TBPD	0.100	isolated	0	110
(44)	$2\,C_{60}\cdot$ BNTTF$\cdot$ PhMe	0.099	3*D* framework	7	110

Table 2 (continued).

CSD Refcode or (Ref.)	Formula [a]	*R*-factor	Motif	MCN (see [b])	*T* /K
Solvates and molecular complexes					
(44)	$2\,C_{60}\cdot EDT(DET)TTF$	0.136	3*D* framework	7	110
(45)	$C_{60}\cdot 2\,PyZnTPP\cdot PhMe\cdot Cp_2Fe$	0.099	isolated	0	110
(45)	$C_{70}\cdot 2\,PyZnTPP\cdot PhMe\cdot 0.5\,C_2HCl_3$	0.116	"	0	110
(46)	$2\,C_{60}\cdot TPyP\cdot 4\,ZnTPP\cdot 1.75\,PhCN$	0.087	island	1	110
Ionic complexes with neutral fullerene					
PIBQOG	$C_{60}\cdot 4\,NaH$	0.086	–	–	295
HIFCOO	$C_{60}\cdot 5\,AgNO_3$	0.149	cubic framework	6	140
XAYXOK	$C_{60}\cdot BEDT\text{-}TTF^+\cdot I_3^-$	0.034	hexagonal layers	6	90
GUDZEK	$C_{60}\cdot FeTPP^+\cdot(C_6F_5)_4B^-\cdot 2.5\,(o\text{-}C_6H_4Cl_2)$	0.093	chains	2	203
Radical-ion salts and fullerides					
KUGGIC	$C_{60}^-\cdot TDAE^+$	0.086	cubic framework	6	295
GEXQUV	$C_{60}^-\cdot(PhMe)_2Cr^+\cdot CS_2$	0.138	honeycomb	6	150
MOBWUV	$C_{60}^-\cdot(PhMe)_2Cr^+$	0.077	distorted simple cubic	6	235
PUKHAE	$C_{60}^-\cdot Cp_2Co^+\cdot CS_2$	0.151	3*D* framework	8	123
ZESHIO	$C_{60}^-\cdot(Me_5Cp)_2Ni^+\cdot CS_2$	0.045	tetragonal layers	4	150
LAZPAD	$C_{60}^-\cdot 2\,Ph_4P^+\cdot I^-$	0.047	isolated	0	295
YEBDUE	$C_{60}^-\cdot 2\,Ph_4P^+\cdot Cl^-$	0.051	"	0	295
YUXCAV	$C_{60}^-\cdot 2\,Ph_4P^+\cdot Br^-$	0.083	"	0	295
YUXCEZ	$C_{60}^-\cdot 2\,Ph_4As^+\cdot Cl^-$	0.126	"	0	295
POFWEM	$C_{70}^-\cdot 2\,Ph_4P^+\cdot I^-$	0.210	"	0	295
FULLER	$C_{60}^-\cdot Cs^+$	0.043	bcc	8	295
YEXLIW	$C_{60}^-\cdot K^+$	–	–	–	295
HEJDEF	$C_{60}^{n-}\cdot n\,Na^+\cdot m\,THF$	–	–	–	295
HEJDIJ	$C_{60}^{n-}\cdot n\,K^+\cdot m\,THF$	–	–	–	295
PAVLAZ	$C_{60}^-\cdot(Ph_3P)_2N^+$	0.020	–	–	295
WEZYEF	$C_{60}^{2-}\cdot 2\,(Ph_3P)_2N^+$	0.042	isolated	0	108
NAPPOJ	$C_{60}^{2-}\cdot 2\,PhCH_2NMe_3^+\cdot 3\,NH_3$	0.052	tetragonal layers	4	113
TUQTAA	$C_{60}^{2-}\cdot 2\,CryptK^+\cdot 4\,PhMe$	0.109	isolated	0	113
PUHJIL	$C_{60}^{2-}\cdot Mn(NH_3)_6^{2+}\cdot 6\,NH_3$	0.035	tetragonal layers	4	113
RAJNIZ	$C_{60}^{2-}\cdot Co(NH_3)_6^{2+}\cdot 6\,NH_3$	0.053	the same	4	143
NUHJUV	$C_{60}^{2-}\cdot Ni(NH_3)_6^{2+}\cdot 6\,NH_3$	0.037	"	4	113
RAJNOF	$C_{60}^{2-}\cdot Zn(NH_3)_6^{2+}\cdot 6\,NH_3$	0.079	"	4	143
PUHJOR	$C_{60}^{2-}\cdot Cd(NH_3)_6^{2+}\cdot 6\,NH_3$	0.047	"	4	113
NUSVAY	$C_{60}^{2-}\cdot Ba(NH_3)_7^{2+}\cdot NH_3$	0.023	cubic framework	6	113
EBOYOJ	$C_{70}^{2-}\cdot Ba(NH_3)_9^{2+}\cdot 7\,NH_3$	0.119	diamond-like	4	143
TADQAQ	$C_{60}^{3-}\cdot 3\,K^+\cdot 14\,THF$	0.109	isolated	0	140
YAPRAI	$C_{60}^{3-}\cdot NH_3\cdot 3\,K^+$	0.031	distorted fcc	12	295
GORXUG	$C_{60}^{3-}\cdot 3\,CrownK^+\cdot 2\,PhMe$	0.082	isolated	0	110
WEHRUW	Na_2RbC_{60}	0.129	fcc	12	27
WESYEY	Na_2CsC_{60}	0.052	"	12	20
XASKUX	$RbCs_2C_{60}$	–	"	12	295
ICECEY	$Sm_{2.75}C_{60}$	–	"	12	200
QUHYOH	$K_3Ba_3C_{60}$	0.075	bcc	8	10
(47)	$C_{60}^-Cs^+\cdot CoTPP\cdot 1.64\,PhCN\cdot 0.36\,(o\text{-}C_6H_4Cl_2)\cdot CH_3CN$	0.121	island	1	110
(38)	$C_{59}N^+Ag(CB_{11}H_6Cl_6)_2^-\cdot 3\,(o\text{-}C_6H_4Cl_2)$	0.069	isolated	0	223
(48)	$Eu_{3-x}C_{70}$	see [c]	fcc	12	298
(48)	$Eu_{9-x}C_{70}$	see [c]	"	12	298
Binary compounds					
VUWFUO	$C_{60}O$	0.096	isolated	0	19
YOSHIX	$C_{60}O_2$	0.052	"	0	295
CELZAU	$(C_{60})_2O\cdot 2\,CoOEP\cdot 1.2\,CHCl_3\cdot 0.8\,C_6H_6$	0.151	"	0	130
EBUFAI	$C_{60}F_{48}\cdot 2\,(1,3,5\text{-}C_6H_3Me_3)$	0.051	"	0	108
JUHJIF	$C_{60}Br_{24}\cdot Br_2$	0.038	"	0	143
MEBBOK	$C_{60}F_{18}O\cdot PhMe$	0.052	see [d]	see [d]	173
SUDVIW	$C_{60}Br_8\cdot 2\,Br_2$	0.137	–	–	173
SUDVOC	$C_{60}Br_6\cdot Br_2$	0.092	–	–	173
XAFLIZ	$C_{60}F_{18}\cdot PhMe$	0.049	see [d]	see [d]	100
XAPSEM	$C_{60}F_{17}CF_3\cdot 2\,PhMe$	0.066	see [d]	see [d]	173
ACULUF	$C_{60}Me_4PhO_2(OH)$	0.045	honeycomb	7	173

Table 2 (continued).

CSD Refcode or (Ref.)	Formula [a]	*R*-factor	Motif	MCN (see [b])	*T*/K
Binary compounds					
ACUMAM	$C_{60}Me_6$	0.123	puckered hexagonal layers	7	173
(49)	$C_{70}Br_{10}$	0.055	3*D* framework	5	153
(49)	$C_{70}Br_{10} \cdot 3\,Br_2$	0.139	honeycomb	5	170
σ-Derivatives					
AFICAT	$C_{60}C_2(CN)_4O \cdot HMTTF$	–	–	–	295
BAVKUE	$C_{60}Mcbcd \cdot CHCl_3 \cdot 0.5\,C_6H_{14}$	0.049	puckered layers	5	120
BIFFUR	$C_{60}Ppo \cdot CS_2$	0.084	–	–	295
CODVOG	T_h-$C_{60}(Tmp)_6 \cdot 4\,H_2O$	0.071	isolated	0	100
COFCIJ	D_3-$C_{60}(Tmp)_6 \cdot 0.11\,C_3H_6O \cdot 4\,H_2O$	0.053	"	0	148
DEXSOO	$C_{60}DMalK^+PF_6^- \cdot CH_2Cl_2 \cdot 0.5\,C_6H_6$	0.078	double chains	3	243
DIPWEE	$C_{60}(Fl)_2 \cdot TBrCalix[3] \cdot 2\,PhMe$	0.081	isolated	0	295
FERYOQ	$C_{60}(CN)(Tmopp) \cdot PhMe$	0.046	honeycomb	6	123
GASFEL	$(C_{60}Mal_5CPy_2)_2[Pt(PPh_3)_2]_2^{4+} \cdot 4\,(CF_3SO_3^-)$	0.092	isolated	0	295
GASFIP	$C_{60}Mal_5CPy_2 \cdot C_6H_6 \cdot 1.2\,CH_3CO_2Et$	0.096	"	0	295
HATGOY	$C_{60}(Dmxy) \cdot 0.5\,C_6H_6$	0.038	3*D* framework	6	295
HELWEA	$C_{60}C(Ph)C_6H_3(MeO)_2 \cdot 2\,CHCl_3$	0.062	diamond-like	4	295
HERNAT	$C_{60}C(C_4SiMe_3)_2 \cdot 0.5\,CS_2$	0.053	honeycomb	5	100
HERNEX	$C_{60}C(C_4SiMe_3)_2 \cdot 2\,PhMe$	0.049	graphite-like	3	100
HUCNAU	$C_{60}PPZnTPP \cdot C_7H_{16}$	0.092	chains	2	218
JUTNAN	$C_{60}Dpbdm \cdot o$-$C_6H_4Cl_2$	0.098	layers	5	295
LIKGER	$C_{60}Mal \cdot CHCl_3$	0.045	3*D* framework	8	193
NACVIW	$C_{60}CHE \cdot 2\,(o$-$C_6H_4Cl_2)$	0.055	cubic framework	6	178
NACVIX	$C_{60}Ant$	–	–	–	295
NAFDAZ	$C_{60}[Si(SiMe_3)_3]_2 \cdot CS_2$	0.062	double chains	4	295
NAFKUA	$C_{60}(Pip)_2 \cdot 0.5\,CH_2Cl_2$	0.063	3*D* framework	6, 7	295
NAFLAH	$C_{60}(Pip)_2 \cdot 0.5\,Et_2O$	0.052	honeycomb	6, 8	130
NARZIP	$(C_{60})_2 \cdot 4\,(o$-$C_6H_4Cl_2)$	0.067	layers	5	295
NAWLAY	$C_{60}Mpc \cdot 0.5\,C_6H_6$	0.043	double layers	7, 8	120
NISNOS	$C_{60}C(C_6H_4Br)_2$	0.033	hexagonal layers	6	100
NITGAY	$C_{60}(Fl)_4 \cdot 3\,PhMe$	0.061	chains	2	203
PIPNIL	$C_{60}AIz \cdot CS_2$	0.060	3*D* framework	6	173
RERLAB	$C_{60}AIz \cdot PhMe$	0.040	separated hexagonal layers	6	253
QAJMET	$C_{60}(m$-$XMal)_3 \cdot 3.5\,CH_2Cl_2$	0.085	isolated	0	228
QAWRUB	$C_{60}(CH_2Ph)_4 \cdot CS_2 \cdot 0.5\,C_6H_{14}$	0.062	tetragonal layers	4	223
QAWSAI	$C_{60}(CH_2Ph)_4 \cdot 2\,CS_2$	0.063	puckered graphite	3	223
QICZIL	$(C_{60}O)_2[NMe(CH_2)_3NMe]_4 \cdot 2\,CHCl_3$	0.198	puckered layers	3–4	295
RAWQAH	$C_{60}Ph_5Tl \cdot 2.5\,THF$	0.079	chains	2	295
RAZZUN	$C_{60}Bqd \cdot C_6H_6$	0.025	–	–	295
REBLAL	$C_{60}SPPIz \cdot 2\,(o$-$C_6H_4Cl_2)$	0.056	puckered graphite	3	148
RECCIL	$C_{60}TPPPyr \cdot CHCl_3$	0.080	island	1	163
REDJEP	$C_{60}Epp$	0.062	3*D* framework	10	295
RERKUU	$C_{60}BCIz \cdot PhMe$	0.047	honeycomb	7	295
RUNQEW	$C_{60}(Mal)_4 \cdot 2\,CHCl_3$	0.041	columns	2	100
TEKRIK	$C_{60}Mpd \cdot CS_2$	0.045	honeycomb	7	295
TIMTIS	$[C_{60}C(C_2SiPr^i_3)]_2C_4 \cdot 2\,PhMe$	0.047	"	5	100
TIYGAJ	$C_{60}DmPhe \cdot CS_2$	0.046	–	–	295
TODBUJ	$C_{60}Trz$	0.091	3*D* framework	9	193
TOPROF	$C_{60}(o$-$XMal) \cdot CHCl_3$	0.064	puckered layers	5	295
TOWQOL	$C_{64}H_4Fe(CO)_3 \cdot 2.5\,CS_2$	0.060	cubic framework	6	156
TUJSIA	$C_{60}S_2Fe_2(CO)_6 \cdot 0.25\,PhMe \cdot 0.5\,C_5H_{12}$	0.057	3*D* framework	6	198
TUJXEB	$C_{60}(H)Fl \cdot 2\,C_6H_6$	0.049	puckered tetragonal layers	4	295
TUQJIY	$C_{60}Dtdm \cdot CS_2$	0.056	3*D* framework	7	295
VEHQII	$C_{60}C(COOH)Pcp$	0.167	puckered tetragonal layers	4	295
VUBBEZ	$C_{60}OsO_4(4$-$Bu^tPy)_2$	0.103	–	–	295
WECZAF	$C_{60}Me_5O_2(OH)$	0.075	honeycomb	8	173
YAPWIV	$C_{60}Hex \cdot 1.5\,PhCl$	0.116	double chains	4	295
YIRXEC	$C_{60}CCpdm \cdot 3\,C_6H_6$	0.063	graphite-like	3	295
ZAKMUT	$C_{60}(Mal)_3Mbde \cdot 2\,C_6H_6$	0.049	isolated	0	233
ZEDWEK	$C_{60}(Mal)_6 \cdot 2\,PhBr$	0.066	"	0	295
ZIHJOP	$C_{60}Pip \cdot 1.5\,CH_2Cl_2$	0.060	tetragonal layers	8	130
ZIHJUV	$C_{60}(Pip)_2 \cdot 0.7\,CH_2Cl_2 \cdot 0.3\,Et_2O$	0.098	the same	4	130
ZIJCOK	$C_{60}(CN)_2 \cdot 2\,(o$-$C_6H_4Cl_2)$	0.084	cubic framework	6	295
ZUHSEA	$C_{60}C(C_6H_4OMe)_2$	0.038	tetragonal layers	4	295

Table 2 (continued).

CSD Refcode or (Ref.)	Formula [a]	*R*-factor	Motif	MCN (see [b])	*T*/K
σ-Derivatives					
ZUSSUB	$C_{64}H_4CoCp \cdot PhMe$	0.076	puckered hexagonal layers	6	156
BUBQIY	$(C_{60})_2(Mal)_{10} \cdot 4\,PhCl$	0.075	island	1	103
NEPHAR	$C_{60}Phd \cdot 2\,CS_2$	0.087	diamond-like	4	91
UBIJAQ	$C_{60}(Ant)_2 \cdot 1.5\,CS_2 \cdot C_6H_{14}$	0.068	chains	2	218
UBIJEU	$C_{60}(Ant)_2 \cdot 1.5\,CS_2$	0.053	double chains	3	218
VODZIX	$C_{60}(MalBr)_3F_{15} \cdot PhMe$	0.049	island	1	173
VOKFOQ	$C_{60}(1\text{-}MeAnt) \cdot 2\,CHCl_3$	0.067	columns	2	223
XARVAN	$C_{70}(DMal) \cdot 6\,CHCl_3$	0.077	chains	2	233
SERDUO	$C_{70}Phe \cdot PhMe$	0.089	3*D* framework	8	295
REFTOL	$C_{70}TMOIz \cdot 0.5\,CS_2$	0.046	"	10	170
CELQUF	$C_{70}CCl_2 \cdot 0.45\,C_5H_{12} \cdot 0.05\,PhMe$	0.089	"	10, 11	110
GIZCIB	$C_{70}(C_6H_4CF_3)_3Tl \cdot o\text{-}C_6H_4Cl_2$	0.085	hexagonal layers	6	295
ZADQUQ	b-C_{70}Dmxy $\cdot 2\,CS_2$	0.045	3*D* framework	6	193
ZADRAX	d-C_{70}Dmxy $\cdot 2\,CS_2$	0.049	cubic framework	6	100
(50)	$C_{60}Me_5Ph_5O_3(OH)_2 \cdot PhCl$	0.145	puckered graphite	–	173
(51)	$C_{62}(p\text{-}C_6H_4Me)_2 \cdot CHCl_3 \cdot CS_2$	0.059	columns	2	100
π-Derivatives					
HADSIO	$C_{60}Pd(PPh_3)_2$	0.094	puckered layers	5	193
RACTUK	$C_{60}Pt(PPh_3)_2$	0.069	–	–	295
PECTAS	$C_{60}Pt(PPh_3)_2 \cdot THF$	0.059	–	–	203
BEJKUW	$C_{70}Pd(PPh_3)_2 \cdot CH_2Cl_2$	0.093	diamond-like	4	130
GUDNOI	$C_{60}Rh(PPh_2CH_2)_3CCH_3$	0.072	island	1	295
HAJYIA	$C_{60}Rh(CO)H(PPh_3)_2 \cdot 3.27\,CH_2Cl_2$	0.072	3*D* framework	2, 4	123
KOKXUD	$C_{60}Ir(CO)Cl(PPh_3)_2 \cdot 5\,C_6H_6$	0.067	island	1	130
WIHFUO	$C_{60}OIr(CO)Cl(PPh_3)_2 \cdot 0.53\,CHCl_3 \cdot 4.47\,C_6H_6$	0.057	isolated	0	123
ZEKXAO	$C_{60}O_2Ir(CO)Cl(PPh_3)_2 \cdot 4.8\,C_6H_6$	0.055	"	0	130
ZOQBUC	$C_{60}OIr(CO)Cl(AsPh_3)_2 \cdot 0.18\,CHCl_3 \cdot 4.82\,C_6H_6$	0.066	"	0	123
JOHGOC	$C_{70}Ir(CO)Cl(PPh_3)_2 \cdot 2.5\,C_6H_6$	0.068	graphite-like	3	120
TUFTIX	$C_{70}OIr(CO)Cl(PPh_3)_2 \cdot 5\,C_6H_6$	0.099	"	3	125
SUMZUV	$C_{84}Ir(CO)Cl(PPh_3)_2 \cdot 4\,C_6H_6$	0.036	diamond-like	4	295
KUFHEY	$C_{60}Ir(CO)Cl(podp)_2$	0.066	chains	2	130
LIXTUH	$C_{60}TiCp_2 \cdot PhMe$	0.076	3*D* with channels	6	120
MAZBIY	$C_{60}Mo(CO)_3(dppbz) \cdot 3\,THF$	0.051	graphite-like	3	295
MAZBOE	$C_{60}W(CO)_3(dppbz) \cdot 3\,THF$	0.068	"	3	295
NOWSOH	$C_{60}Mo(CO)_2(Phen)(bml) \cdot 2\,C_6H_6 \cdot C_5H_{12}$	0.125	chains	2	295
NOWSUN	$C_{60}W(CO)_2(Phen)(bml) \cdot 2\,C_6H_6 \cdot C_5H_{12}$	0.087	"	2	295
SUXGAT	$C_{70}Mo(CO)_2(Phen) \cdot 2\,Pr^iOH \cdot 2.5\,H_2O$	0.095	diamond-like	4	173
MINSAD	$(C_{60})_2W(CO)_2(BBPy) \cdot C_5H_{12} \cdot 3\,CS_2$	0.085	honeycomb	5, 6	123
MINSEH	$(C_{60})_2Mo(CO)_2(BBPy) \cdot C_5H_{12} \cdot 4\,CS_2 \cdot H_2O$	0.098	"	5, 6	123
POKMOR	$C_{60}Rh(DMPy)_2(acac) \cdot C_6H_6$	0.057	diamond-like	4	295
POQJOU	$C_{60}W(dppe)(CO)_3 \cdot 2\,(o\text{-}C_6H_4Cl_2) \cdot C_6H_{12}$	0.051	island	1	198
PUKWAT	$C_{60}Ru(NO)Cl(PPh_3)_2 \cdot 5\,C_6H_6$	0.061	isolated	0	295
PUNDOR	$C_{60}Mo(dppe)(CO)_3 \cdot CS_2$	0.041	chains	2	198
PUNDUX	$C_{70}Mo(dppe)(CO)_3 \cdot 3\,CHCl_3$	0.082	double chains	4	198
XAWHUY	$C_{60}Mn(CO)_4^-(PPh_3)_2N^+ \cdot THF$	0.136	puckered tetragonal layers	4	173
TIBJAP	$C_{60}Pt(dodppb) \cdot C_8H_{14}$	0.065	diamond-like	4	148
LADLAD	$C_{60}[Ir(CO)Cl(PPhMe_2)_2]_2 \cdot C_6H_6$	–	isolated	0	120
LADLEH	$C_{60}[Ir(CO)Cl(PPhMe_2)_2]_2 \cdot 2\,C_6H_6$	0.034	columns	2	123
XEHYOY	$(C_{60})_2Ir_2(CO)_2Cl_2(dpph)_2 \cdot 4\,C_6H_6 \cdot 2\,CH_2Cl_2$	0.053	chains	2	130
YEMVOB	$(\eta^2,\eta^2\text{-}C_{60})[Ir(CO)Cl(PMe_3)_2]_2 \cdot 2\,C_6H_6$	0.065	isolated	0	123
YEMVUH	$(\eta^2,\eta^2\text{-}C_{60})[Ir(CO)Cl(PEt_3)_2]_2 \cdot C_6H_6$	0.073	columns	2	123
PUHXUL	$(\eta^2,\eta^2\text{-}C_{60})Ir_2(MeO)(PhO)(C_8H_{12})_2 \cdot CH_2Cl_2$	0.110	tetragonal layers	4	295
PUKWEX	$(\eta^2,\eta^2\text{-}C_{60})Re_2(PMe_3)_4 \cdot 1.5\,C_6H_6$	0.034	graphite-like	3	295
VURTEH	$(\eta^2,\eta^2\text{-}C_{70})[Ir(CO)Cl(PPhMe_2)_2]_2 \cdot 3\,C_6H_6$	0.051	chains	2	130
ZISJOA	$(\eta^2,\eta^2\text{-}C_{60})Ru_2(Me_5Cp)_2(H)(Cl) \cdot PhMe$	0.040	graphite-like	3	295
ZISJUG	$(\eta^2,\eta^2\text{-}C_{60})Ru_2(Me_5Cp)_2(Cl)_2 \cdot 2\,PhMe$	0.045	"	3	295
TOPNER	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})Ru_3(CO)_9 \cdot CS_2$	0.076	double hexagonal layers	7	295
NAXNIJ	$(b,b,d\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{70})Ru_3(CO)_9 \cdot CS_2$	0.086	3*D* with channels	8	198
PUKBIG	$(\eta^2\text{-}C_{60})Os_3(CO)_{11} \cdot CH_2Cl_2$	0.064	diamond-like	4	295
OBINIW	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})Os_3(CO)_8(BIC) \cdot 0.25\,CS_2$	0.069	puckered hexagonal layers	5, 6	293
OBINOC	$(\sigma,\eta^2,\sigma\text{-}C_{60})Os_3(CO)_8(BIC)_2 \cdot CS_2$	0.045	puckered graphite	3	293

Table 2 (continued).

CSD Refcode or (Ref.)	Formula [a]	*R*-factor	Motif	MCN (see [b])	*T* /K
π-Derivatives					
OBINUI	$(\sigma,\eta^2,\sigma\text{-}C_{60})Os_3(CO)_8(BIC)_2$	0.078	puckered graphite	3	293
HISVAG	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})Os_3(PPh_3)(CO)_8 \cdot 1.5\,CS_2$	0.063	puckered tetragonal layers	4	295
MAZLUU	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})Os_3(PMe_3)_2(CO)_7 \cdot CS_2$	0.065	hexagonal layers	6	295
MAZMAB	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})Os_3(PMe_3)_3(CO)_6 \cdot 2\,CH_2Cl_2$	0.065	graphite-like	3	295
AFOXEY	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})Os_3(BIC)_2(PPh_3)(CO)_7 \cdot o\text{-}C_6H_4Cl_2$	0.041	chains	2	298
AFOXIC	$(\eta^2,\eta^2\text{-}C_{60})Os_3(PPh_3)(PPh_2)(C_{12}H_{13}N_2)(CO)_6$	0.065	"	2	233
AFOXOI	$(\sigma,\eta^2,\sigma\text{-}C_{60})Os_3(BIC)_2(PMe_3)(CO)_7 \cdot CS_2$	0.076	tetragonal layers	4	233
MOCPID	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})Re_3(BIC)(CO)_8 \cdot CS_2$	0.053	diamond-like	4	233
MOHYEN	$(\sigma,\eta^2,\sigma\text{-}C_{60})Os_3(BIC)(CO)_9 \cdot 0.5\,CS_2$	0.082	puckered layers	5, 6	233
YAPXOC	$C_{60}[Ir_2Cl_2(C_8H_{12})_2]_2 \cdot 2\,C_6H_6$	0.032	columns	2	295
ZOHVOH	$C_{70}[Pt(Ph_3P)_2]_4 \cdot 6.5\,C_6H_6 \cdot 0.5\,CH_3OH$	0.074	isolated	0	130
MEKXOP	$(\eta^2,\eta^2\text{-}C_{60})Os_5C(CO)_{12}PPh_3$	0.061	double chains	4	295
MEKYAC	$(\eta^2,\eta^2\text{-}C_{60})Os_5C(CO)_{11}PPh_3 \cdot CS_2 \cdot 0.5\,H_2O$	0.120	puckered layers	5	295
MEKXUV	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})Os_5C(CO)_{11}(BIC)PPh_3 \cdot 0.5\,CS_2$	0.140	double chains	4	295
MEKYEG	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})Os_5C(CO)_{11}(BIC)PPh_3$	0.074	the same	4	295
NOGNUS	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})Ru_5C(CO)_{11}PPh_3 \cdot 1.5\,CS_2$	0.069	puckered layers	5	198
GAQCEG	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})Ru_5C(CO)_{10}(dppm) \cdot CH_2Cl_2$	0.131	graphite-like	3	198
GAQCIK	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})Ru_5C(CO)_{10}(dppfc) \cdot CH_2Cl_2$	0.102	chains	2	198
MIDMIV	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})Ru_5C(CO)_{10}(PPh_3)(BIC) \cdot 2\,CS_2$	0.058	"	2	233
NOGPAA	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})Ru_6(CO)_{12}(dppm) \cdot 3\,CS_2$	0.085	"	2	295
NAXNOP	$C_{70}[Ru_3(CO)_9]_2 \cdot 1.5\,CS_2$	0.085	puckered layers	5	198
GAQCUW	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})\,PtRu_5C(CO)_{11}(dppm) \cdot 2\,CS_2$	0.044	island	1	198
XIJQEM	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})Rh_6(dppm)_2(CO)_9$	0.104	"	1	293
XIJQIQ	$(\eta^2,\eta^2,\eta^2\text{-}C_{60})_2Rh_6(dppm)_2(BIC)(CO)_5 \cdot$ $\cdot 1.5\,(o\text{-}C_6H_4Cl_2) \cdot 2.75\,CS_2$	0.085	puckered layers	3	293
KOLSOT	$C_{60}[Pt(Ph_3P)_2]_6$	0.033	isolated	0	203
(52)	$\eta^2\text{-}C_{60}Ir(Cbpp)(Bu^tNC)_2 \cdot 4\,PhMe$	0.045	chains	2	190
(52)	$\sigma\text{-}C_{60}IrO_2(Cbpp)(Bu^tNC)_2 \cdot 3.67\,CHCl_3$	0.065	loose layers	3	100
Endohedral metallofullerenes and their derivatives					
BOJNIX	$Sc_3N@C_{80} \cdot CoOEP \cdot 1.5\,CHCl_3 \cdot 0.5\,C_6H_6$	0.224	chains	2	130
BEZCUE	$ErSc_2N@C_{80} \cdot CoOEP \cdot 0.3\,CHCl_3 \cdot 1.5\,C_6H_6$	0.087	"	2	90
QOFZIU	$Sc_3N@C_{78} \cdot CoOEP \cdot 0.3\,CHCl_3 \cdot 1.5\,C_6H_6$	0.111	"	2	110
XILSUG	$Sc_3N@C_{80}Dmxy \cdot 2\,C_6H_6$	0.064	puckered hexagonal layers	5	91
XIMKOT	$Er_2@C_{82} \cdot CoOEP \cdot 1.4\,C_6H_6 \cdot 0.3\,CHCl_3$	0.148	chains	2	113
(16)	$Sc_3N@C_{68} \cdot NiOEP \cdot 2\,C_6H_6$	0.094	isolated	0	91

[a] Abbreviated names of molecules and ligands are explained in Table 3. [b] Molecular coordination number. [c] According to powder X-ray diffraction. [d] Not applicable due to substantial nonsphericity of the carbon cage.

Table 3. Molecules and ligands as comonents of fullerene derivatives.

Abbreviation	Formula	Name
Neutral molecules and ligands		
acac	$C_5H_7O_2$	acetylacetonate
AT	$C_{19}H_{13}N$	azatriptycene
BBPy	$C_{20}H_{24}N_2O_4$	4,4′-bis(n-butoxycarbonyl)-2,2′-bipyridyl
BDMT-TTeF	$C_{14}H_{12}S_2Te_4$	bis(dimethylthieno)tetrathiafulvalene
BEDTB(EDT)	$C_{20}H_{16}S_{16}$	bis(ethylenedithio)bis(ethylenedithiotetrathiafulvalene)
BEDT-TTF	$C_{10}H_8S_8$	bis(ethylenedithio)tetrathiafulvalene
bml	$C_{12}H_{20}O_4$	di(n-butyl) maleate
BIC	C_8H_7N	benzyl isocyanide
BNDTY	$C_{22}H_{12}S_4$	bi(naphtho[1,8-*d*,*e*]-1,3-dithiin-2-ylidene)
BNTTF	$C_{22}H_{16}S_4$	binaphthotetrathiafulvalene
BPZnOEP	$C_{108}H_{124}N_8O_4Zn_2$	μ2-5,5′:15,15′-bis[1,6-bis(*m*-phenyleneoxy)hexane]bis(2,3,7,8,12,13,17,18-octaethyl-porphyrinato) zinc
BTX	$C_{26}H_{18}Te_2$	9,9′-*trans*-bitelluraxanthenyl
Calix[6]	$C_{42}H_{36}O_6$	calix[6]arene
Crown	$C_{12}H_{24}O_6$	18-crown-6
Crypt	$C_{18}H_{36}N_2O_6$	2,2,2-cryptand
CTV	$C_{27}H_{30}O_6$	cyclotriveratrylene

Table 3 (continued).

Abbreviation	Formula	Name
Neutral molecules and ligands		
DAN	$C_{28}H_{20}$	9,10-[9,10]anthracenoanthracene
DBTTF	$C_{14}H_8S_4$	dibenzotetrathiafulvalene
DIDMCalix[5]	$C_{38}H_{34}I_2O_5$	3,16-diiodo-10,22,28-trimethylcalix[5]arene
Diox	$C_4H_8O_2$	dioxane
DMPy	C_7H_9N	3,5-dimethylpyridine
DMTEDT-TTF	$C_{10}H_{10}S_8$	di(methylthio)ethylenedithiotetrathiafulvalene
dodppb	$C_{31}H_{32}O_2P_2$	*O*,*O*′-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
dppbz	$C_{30}H_{24}P_2$	bis(diphenylphosphino)benzene
dppe	$C_{26}H_{24}P_2$	bis(diphenylphosphino)ethane
dppfc	$C_{34}H_{28}P_2Fe$	bis(diphenylphosphino)ferrocene
dpph	$C_{31}H_{34}P_2$	bis(diphenylphosphino)heptane
dppm	$C_{25}H_{22}P_2$	bis(diphenylphosphino)methane
DTDSeF	$C_8H_8S_3Se_2$	2-(4-thioxo-1,3-dithiolane-5-ylidene)-4,5-dimethyl-1,3-diselenol
EDT(DET)TTF	$C_{12}H_{14}S_8$	ethylenedithio(diethylthio)tetrathiafulvalene
HMTPH	$C_{24}H_{24}O_6$	hexamethoxytriphenylene
HMTTF	$C_{12}H_{12}S_4$	hexamethylenetetrathiafulvalene
MDT-TTF	$C_8H_4S_8$	methylenedithiotetrathiafulvalene
ODAPz	$C_{32}H_{48}N_{16}$	octakis(dimethylamino)porphyrazin
OEP	$C_{36}H_{40}N_4$	octaethylporphyrin
OMCTD	$C_{26}H_{30}N_4$	5,14-dihydro-2,3,6,8,11,12,15,17-octametyldibenzotetraaza(14)annulene
OMTTF	$C_6H_{16}S_4$	octametylenetetrathiafulvalene
OPCTSil	$C_{48}H_{40}O_4Si_4$	octaphenylcyclotetrasiloxane
PBMP	$C_{17}H_{14}N_2O_2$	4-benzoyl-3-methyl-1-phenylpyrazol-5-one
PBzCalix[5]	$C_{70}H_{60}O_5$	pentabenzylcalix[5]arene
biCalix[5]	$C_{70}H_{58}O_{10}$	bicalix[5]arene
PdBPPyP	$C_{134}H_{150}N_{10}Pd_3Cl_2$	bis[μ_2-5-(3-pyridyl)-10,15,20-tris(3,5-dibutylphenyl)porphyrin]dichlorotripalladium
Calix[5]	$C_{35}H_{30}O_5$	calix[5]arene
Phen	$C_{12}N_2H_8$	1,10-phenanthroline
PMCalix[5]	$C_{40}H_{40}O_5$	5,11,17,23,29-pentamethylcalix[5]arene
podp	$C_{26}H_{23}OP$	4-benzyloxybenzyldiphenylphosphine
Py	C_5H_5N	pyridine
TAP	$C_{92}H_{76}N_2$	tetrakis(2,3,6,7-tetramethyl-9,10-dihydro[9,10]anthracene)porphyrin
TBBCN	$C_{63}H_{42}O_{12}$	tris(4,5-dibenzoyloxybenzo)[*a*,*d*,*g*]cyclonona-1,4,7-triene
TBPD	$C_{34}H_{32}N_4$	*N,N,N',N'*-tetrabenzyl-*p*-phenylenediamine
TBrCalix[3]	$C_{24}H_{21}Br_3O_6$	tribromotris(oxadihomo)calix[3]arene
TBTPCalix[4]	$C_{40}H_{44}Br_4O_4$	5,11,17,23-tetrabromo-25,26,27,28-tetra-*O*-n-propylcalix[4]arene
TBuCalix[3]	$C_{36}H_{48}O_6$	tri-*tert*-butyltris(oxadihomo)calix[3]arene
TBuCalix[3]N	$C_{48}H_{54}O_6$	8,18,28-tributyltris(oxadihomo)calix[3]naphthalene
TBzCalix[3]	$C_{45}H_{42}O_6$	7,15,23-tribenzyltrioxadihomocalix[3]arene
TDAE	$C_{10}H_{24}N_4$	tetrakis(dimethylamino)ethylene
TDBPP	$C_{76}H_{94}N_4$	5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin
TDMPP	$C_{52}H_{44}N_4$	tetrakis(dimethylphenyl)porphyrin
TDZ	$C_4N_4S_6$	3,3′,4,4′-tetrathiabis(1,2,5-thidiazole)
THF	C_4H_8O	tetrahydrofuran
TITBCalix[4]	$C_{56}H_{44}I_4O_4$	5,11,17,23-tetraiodo-25,26,27,28-tetra-*O*-benzylcalix[4]arene
TMCalix[5]	$C_{38}H_{36}O_5$	5,17,23-trimethylcalix[5]arene
TMCTD	$C_{22}H_{22}N_4$	5,7,12,14-tetramethyldibenzotetraaza(14)annulene
TMDTDM-TTF	$C_{12}H_{14}S_6$	tetramethylenedithiodi(methylthio)tetrathiafulvalene
TMPD	$C_{10}H_{16}N_2$	*N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine
TMTSeF	$C_{10}H_{12}Se_4$	tetramethyltetraselenafulvalene
TMTTF	$C_{10}H_{12}S_8$	tetra(methylthio)tetrathiafulvalene
TPBP	$C_{34}H_{24}O_2$	2,2′,6,6′-tetraphenyldipyranylidene
TPivP	$C_{64}H_{66}N_8O_4$	tetrakis(*o*-pivalamido)phenylporphyrin
TPCalix[4]R	$C_{60}H_{56}O_8$	tetra(phenethyl)calix[4]resorcinarene
TPP	$C_{44}H_{28}N_4$	tetraphenylporphyrin
TPyP	$C_{40}H_{28}N_8$	tetrakis(4-pyridyl)porphyrin
Trip	$C_{20}H_{14}$	triptycene
TTF	$C_6H_4S_4$	tetrathiafulvalene
TTolP	$C_{48}H_{36}N_4$	tetra(*p*-tolyl)porphyrin

Table 3 (continued).

Abbreviation	Formula	Name
Substituents		
Ant	$C_{14}H_8$	anthracene-9,10-diyl
Bqd	$C_8H_6O_2$	1,4-benzoquinone-2,3-diyldimethylene
Cbpp	$C_{15}B_{10}H_{22}P$	(diphenylphosphinomethylene)carboranyl
CCpdm	$C_{35}H_{27}Co$	(1,2,3,4-tetraphenylcyclobutadiene)cobaltcyclopentadienyldimethylenediyl
CHE	C_6H_8	cyclohex-2-ene-1,4-diyl
DMal	$C_{32}H_{36}O_{14}$	dibenzo-18-crown-6-3,3′-diyl-bis[(ethoxycarbonyl)methoxycarboranylmethylene]
DmPhe	$C_8H_8O_2$	4,5-dimethoxyphenylene
Dmxy	$C_{10}H_{12}O_2$	dimethoxyxylylene
Dpbdm	$C_{22}H_{20}$	1,4-dimethyl-2,3-diphenylphenylenedimethyldiyl
Dtdm	$C_5H_4S_3$	1,3-dithiole-2-thione-4,5-dimethylenediyl
Epp	$C_6H_8O_2$	1-ethoxycarbonylpropene-1,2-diyl
Fl	$C_{13}H_9$	9-fluorenyl
Hex	$C_{32}H_{38}O_2$	dimethoxy-7,14-dimethyl-7,14-cyclo-6,15:8,13-dimethano-5,16-ethanohexahydro-hexacenediyl
Mal	$C_7H_{10}O_4$	(diethyl malonate)diyl
Mbde	$C_{19}H_{30}O_4$	bis[4-hexyl(diyl)benzyl]malonatediyl
Mcbcd	$C_{13}H_{18}O_2$	7-butyloxycarbonyl-3-methylbicyclo[4.1.0]heptane-2,5-diyl
Mpc	$C_9H_7NO_4$	(4-methoxycarbonylphenyl)carbamate-*N*,*N*-diyl
Mpd	C_9H_9NO	2-(5-methoxyphenyl)-2-azapropane-1,3-diyl
Pcp	$C_{20}H_{16}O_2P$	1-(triphenylphosphonio)acetylide
Phe	C_6H_4	*o*-phenylene
Phd	$C_{20}H_{19}N_5$	6-phenyl-1,4-bis(2-pyridyl)-2,3,5-triazahepta-1,4-diene-1,3-diyl
Ppo	$C_8H_{12}O_2$	8,8-dimethyl-6,10-dioxaspiro[4,5]decane-1,2-diyl
PPZnTPP	$C_{52}H_{38}N_6Zn$	1-(4-pyridyltetraphenylporphyrinatozinc)-2-methyl-2-azapropane-1,3-diyl
Pip	$C_4H_8N_2$	piperazine-1,4-diyl
Tmopp	$C_{12}H_{15}O_5$	(3,4,5-trimethoxyphenylpropionate)-3,3-diyl
XMal	$C_{18}H_{18}O_8$	*o*-phenylenebis[(ethoxycarbonyl)methoxycarbonylmethylene]
Annelated heterocycles		
C_{60}AIz	$C_{75}H_9NO$	3-(9-anthryl)-4,5-dihydroisoxazolofullerene
C_{60}BCIz	$C_{69}H_7NO_3$	3-benzyloxycarbonylizoxazolofullerene
C_{60}SPPIz	$C_{71}H_{13}NO_3S$	3-[*o*-(*tert*-butylsulfonyl)phenyl]isoxazolofullerene
C_{60}TMOIz	$C_{70}H_{11}NO_4$	3-(2,4,6-trimethoxyphenyl)isoxazolofullerene
$C_{60}(Tmp)_6$	$C_{96}H_{78}N_6$	hexakis(2,2,5,5-tetramethylpyrrolidino)fullerene
C_{60}TPPPyr	$C_{107}H_{35}N_5$	1-methyl-2-(tetraphenylporphyrin)-3,4-pyrrolidinofullerene
C_{60}Trz	$C_{64}H_9N_3O_2$	1-(2-methoxyethoxymethyl)triazolofullerene

derivatives of C_{60}, this is equivalent to distances of 9.9 – 10.3 Å between the centres of the adjacent molecules. As a semiquantitative measure of the density of the fullerene packing, it has been proposed [65] to use the dilution parameter defined as

$$\rho = \frac{V_{\text{cell}} - V_{\text{full}}}{V_{\text{full}}}, \qquad (1)$$

where V_{cell} is the unit cell volume and V_{full} is the volume occupied by fullerene molecules within the unit cell. The dilution parameter ρ ranging from 0.33 (for an fcc packing) to ∞ is linked to the commonly adopted partial packing coefficient of fullerene spheres in a crystal

$$\kappa = \frac{V_{\text{full}}}{V_{\text{cell}}}$$

through a simple relation

$$\frac{1}{\kappa} = \rho + 1.$$

An increase in ρ, which corresponds to progressive 'dilution' of fullerene clusters with other (non-fullerene) molecular components in the crystal, typically leads to a change in the packing motif of the carbon clusters $(C_n)_\infty$ at specific threshold values of ρ. For C_{60} derivatives, the typical ranges of various motifs can easily be estimated based on simple geometrical considerations.[65]

Since the overall structure in this type of compound is kept by non-specific van der Waals interactions, many 'guest' molecules that are similar in size and shape to the van der Waals surfaces form analogous structural motifs with similar values of ρ in the fullerene complexes. The crystal structures of the corresponding complexes may belong to different systems and differ significantly in the unit cell parameters. The packing motif $(C_n)_\infty$ in these structures plays the role of a flexible van der Waals matrix thus justifying the utilisation of MCN and ρ as classification criteria.

Solvent molecules often act as 'guests' in molecular complexes of C_n fullerenes. Crystal solvates are often formed upon growth of fullerene crystals from solutions. Some solvents form several solvates with different compositions. For instance, in the case of CCl_4, two solvates with C_{60} : solvent ratios of 1 : 2 (see Ref. 66) and 1 : 13 (see Ref. 67) have been isolated and characterised; $CBrCl_3$ behaves similarly (see Ref. 68).

Buckminsterfullerene is characterised by a relatively good solubility in aromatic hydrocarbons and their non-polar derivatives, but is virtually insoluble in polar solvents (alcohols, esters, *etc*.).[69] Aliphatic hydrocarbons are poor solvents for C_{60}, but nevertheless also form solvates. Solubility curves of fullerene in many solvents manifest a characteristic inflection, sometimes expressed as a distinct maximum. This phenomenon is known as the 'anomalous temperature dependence',[69] although a number of inorganic systems, *e.g*., $Na_2SO_4 - H_2O$, manifest similar changes in the solubility.[70] Initially, this peculiarity of C_{60} was suggestively

Table 4. Structural motifs of fullerene molecules in fullerene molecular complexes.

Type	MCN	Example	Ref.
'Almost dense' three-dimensional frameworks	9–11	$C_{60}\cdot 2/3\,C_8H_{10}$, $C_{60}\cdot C_5H_{12}$	76, 77
Double layers	7–10	$C_{60}Mpc\cdot 0.5\,C_6H_6$	78
Hexagonal layers with trigonal prismatic cavities in-between	6–8	$C_{60}\cdot 2\,P_4$	79
Loose three-dimensional frameworks (spatial honeycombs with channels or diamond-like frameworks)	4–6	$C_{60}\cdot 4\,C_6H_6$	80
Spatially separated closely packed layers	4–6	$C_{70}\cdot 6\,S_8$	26
Loose layers, including graphite-like	3–6	$C_{60}\cdot PdOEP\cdot 1.5\,C_6H_6$	81
Columnar motifs	2–4	$C_{70}\cdot CoOEP\cdot CHCl_3\cdot C_6H_6$	82
Island motifs	0–1	$C_n\cdot 13\,C_6H_{12}$ (n = 60, 70)	67

associated with a phase transition in pure fullerene[69] or with a formation of multi-molecule clusters in solution.[71] Nowadays, it is widely accepted that it is caused by formation of solvates.[72] At a specific temperature T^* (which, for aromatic solvents, typically lies below the boiling point of the solvent), the solvates incongruently melt, *i.e.*, decompose into fullerene and the solvent. According to the calorimetric studies on a number of fullerene–solvent systems, the enthalpy of the incongruent melting is normally 10–50 kJ per mole of fullerene.[73, 74] Properties of solutions of higher fullerenes are, in general, similar to those of C_{60}, but the solubility of, for example, C_{70} in organic media is usually slightly higher than that of buckminsterfullerene.[75]

The major motifs $(C_n)_\infty$ formed by chemically unbound fullerene spheres encountered in structurally characterised molecular complexes of fullerenes are listed in Table 4. For all the substances, the values of the MCN for fullerene molecules are given. The major motifs of the fullerene–'guest' packings are depicted schematically in Fig. 5.

Packing $(C_n)_\infty$, the least diluted by 'guest' molecules, is found in C_{60} solvates with *m*-xylene,[76] mesitylene,[83] and other small molecules of 1,3- and 1,3,5-substituted benzenes (A). These solvates have the stoichiometry $3\,C_{60}\cdot 2\,A$ and reveal an hcp motif of fullerene spheres with 'excised' columns (MCN = 9–10); the solvent molecules are located in the channels (see Fig. 5 *a*).

Among three-dimensional frameworks of fullerene spheres, the motif found in a series of 1:1 C_{60} solvates with pentane, hexane, dichloroethane, trichloroethane and trichloroethylene, is quite typical. In this structural motif, tetragonal dense layers $(C_{60})_\infty$ are stacked in such a way that the close and the closest stacking arrangements are regularly alternating; the solvent molecules occupy cavities (Fig. 6). The formation of characteristic polysynthetic twins with an approximate 10-fold symmetry axis has been reported for all of these solvates.[84] Higher fullerenes C_{82} and $M@C_{82}$ form toluene solvates of the same structural type.[31, 85] Furthermore, a 1:1 bromoform solvate of C_{60} with the closely packed framework structure is known, in which the disordered solvent molecules are located in cavities.[40]

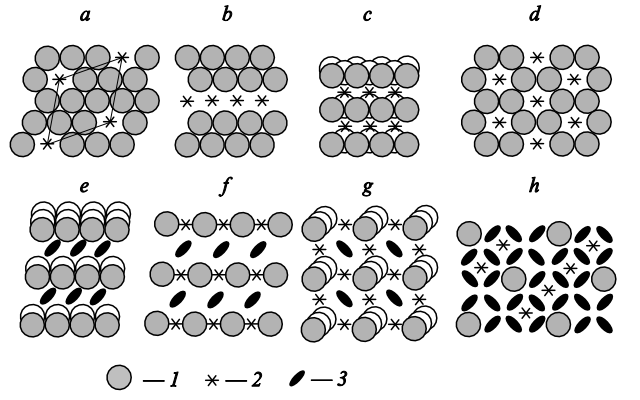


Figure 5. The main packing motifs in molecular complexes of C_{60}.
Motifs: (*a*) 'almost dense', (*b*) double layers, (*c*) closely packed layers, (*d*) framework, (*e*) separated closely packed layers, (*f*) loose layers, (*g*) columns, (*h*) islands (for examples of structures, see Table. 4); (*1*) fullerene, (*2*) solvent molecule, (*3*) 'guest' molecule.

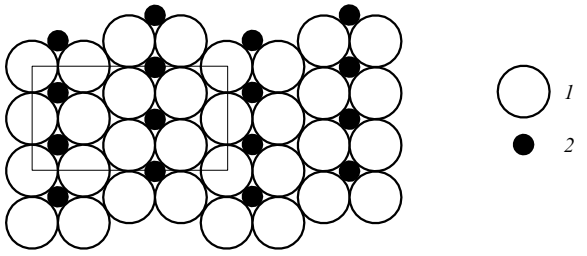


Figure 6. The molecular packing motif in the 1:1 pentane solvate of fullerene.[77]
(*1*) C_{60} molecule, (*2*) pentane molecule; projection of the unit cell is indicated by the rectangle.

Buckminsterfullerene forms an extended series of solvates and molecular complexes with the composition 1:2 [$C_{60}\cdot 2\,A$, where A = P_4,[79] CCl_4,[66] PhBr,[86] Cp_2Fe (see Ref. 87), *etc.*] built up of closely packed hexagonal layers of the fullerene molecules with the 'guest' molecules A in the interlayer space (see Fig. 5 *c*). Such a motif is characterised by the values of MCN = 6–8 and ρ = 0.7–0.8. It is encountered in crystal structures belonging to different systems from hexagonal (*e.g.*, $C_{60}\cdot 2\,P_4$) to triclinic (*e.g.*, $C_{60}\cdot 2\,Cp_2Fe$). In benzene solvates of the fullerene molecular complex with sulfur nitride with the variable composition $C_{60}\cdot 0.67\,S_4N_4\cdot 1.33\,C_6H_6$, half of the 'guest' positions is occupied by the ordered benzene molecules while the other half is statistically occupied by disordered C_6H_6 and S_4N_4 molecules.[88] It is noteworthy that in 1:2 fullerene solvates with bromobenzene and iodobenzene, which are characterised by similar packings but twice larger unit cells, the C_{60} molecules are rotationally disordered in the bromobenzene solvate and fully ordered in the iodobenzene solvate. The distances between the centres of the adjacent C_{60} molecules in the two solvates are 10.16 Å and 9.89 Å, respectively.[41]

A number of 'closely packed' molecular complexes can be prepared by direct intercalation of small molecules into solid fullerene at elevated pressure. In particular, the insertion of oxygen molecules into the octahedral cavities of the fcc packing of fullerene at room temperature and 1 kbar has been detected by NMR.[89] However, the main method of preparation of molecular complexes consists of co-crystallisation of the components from a suitable solvent. Co-crystallisation of buckminsterfullerene with tetrahedral molecules of white phosphorus P_4 from a solution yields the complex $C_{60}\cdot 2\,P_4$ (ρ = 0.82), which has closely packed hexagonal layers of C_{60} molecules. With larger sulfur molecules,

the complex $C_{60} \cdot 2\,S_8$ ($\rho = 1.08$) is formed,[90] which contains a three-dimensional framework of the fullerene molecules with channels. Meanwhile, C_{70} forms a molecular complex with sulfur with the composition 1 : 6 ($\rho = 2.13$)[26] in which layers of the C_{70} molecules are separated by layers of the sulfur molecules (see Fig. 5 *e*). The latter structural motif is also observed in $C_{76} \cdot 6\,S_8$ (see Ref. 27). All the molecular complexes with sulfur reveal short C···S contacts with lengths in the range of 3.20 – 3.50 Å, which apparently stabilise the crystal structures.

Loose layers $(C_{60})_\infty$ (which may be regarded as approximately tetragonal with the MCN = 4) are formed upon insertion of relatively small solvent molecules (C_6H_6, CS_2) from the 'guest' layers into the fullerene layers. For instance, this type of structure is observed for two buckminsterfullerene molecular complexes with tetramethyltetraselenafulvalene, $C_{60} \cdot TMTSeF \cdot 2\,(CS_2)$,[91] and with 9,10-[9,10]-anthracenoanthracene (DAN), $C_{60} \cdot DAN \cdot 3\,C_6H_6$.[92] The latter complex is remarkably stable thus making it possible to isolate buckminsterfullerene from a benzene solution of a mixture of C_{60} and C_{70}. Graphite-like layers with the MCN = 3 are revealed in two benzene solvates of molecular complexes $C_{60} \cdot PdOEP \cdot 1.5\,C_6H_6$[81] and $2\,C_{60} \cdot H_2TPP \cdot 3\,C_6H_6$.[93] Note that another fullerene – tetraphenylporphyrin molecular complex differing from the latter only in the benzene content, *viz*., $2\,C_{60} \cdot H_2TPP \cdot 4\,C_6H_6$ is characterised by a totally different molecular packing involving a three-dimensional framework of the C_{60} molecules with hexagonal channels.

As an example of the columnar motifs, the complex $C_{60} \cdot 2\,(CuTPP)$[93] may be taken, which contains linear chains $(C_{60})_\infty$ with the MCN = 2. In several compounds, more complex one-dimensional motifs are observed, in particular, zigzag chains (*e.g*., in $C_{60} \cdot CTV$, see Ref. 94) or double columns of the fullerene molecules with the MCN = 4 (*e.g*., in $C_{60} \cdot 2\,BEDT\text{-}TTF$, see Ref. 95).

The island packings are typical of complexes with predominating non-fullerene components that separate and isolate the fullerene molecules from each other. In the crystal structures of such complexes, the interaction between fullerene molecules is not a structure-forming factor. Fullerene solvates $C_{60} \cdot 13\,(Solv)$ with cyclohexane, CCl_4 (see Ref. 67) and $CBrCl_3$ (see Ref. 68) are typical examples of such substances. In several cases, the islands are formed by two fullerene cages ('the van der Waals dimers'), which corresponds to the MCN = 1 {*e.g*., in $2\,C_{70} \cdot 9\,[p\text{-}C_6H_4(OH)_2] \cdot 2\,C_6H_6$, see Ref. 96}.

Fullerene forms complexes with inorganic compounds. In the case of molecular inorganic 'guests', such complexes have a normal van der Waals character. As examples, two complexes $C_{60} \cdot 3\,TiCl_4$ and $C_{60} \cdot 3\,C_6H_6 \cdot 2\,Pd_6Cl_{12}$ can be mentioned. The former contains a diamond-like framework,[97] while the latter comprises columns built up of rotationally disordered C_{60} molecules.[98] In some substances, the 'guest' component is represented by charged species of ionic salts, as in $C_{60} \cdot 5\,(Ag^+NO_3^-)$, which reveal a distorted simple cubic packing of the fullerene spheres.[99]

The following large donor molecules forming molecular complexes with fullerenes are worth a special note: derivatives of tetrachalcogenafulvalenes, polyaryl and fused aromatic hydrocarbons, macrocyclic tetraaza-compounds and their complexes with metals, bulky cage molecules (*i.e*., calixarenes, cyclodextrins) with the cavities large enough to accomodate a fullerene sphere. A mismatch in the dimensions of the cavity and the 'guest' in the latter type of compounds results in a decrease in the density and an increase in the structural disorder, which additionally diminishes the accuracy of the structure determination.

Substituted tetrathiafulvalenes (TTF) are prototypical components of radical-ionic salts with aromatic molecules functionalised by strong electrophilic substituents as anions. Planar geometry of both the cation and anion favours their regularly alternating parallel arrangement formed due to the stacking interactions. Nevertheless, systematic single-crystal X-ray diffraction studies have shown that such stacking motifs are not typical

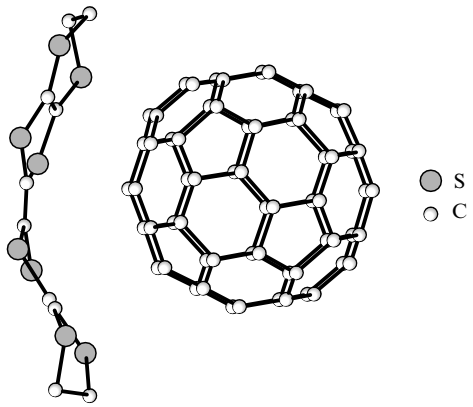


Figure 7. The mutual arrangement of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) and fullerene molecule in the crystal structure of $C_{60} \cdot 2\,BEDT\text{-}TTF$.[95]

of fullerene molecular complexes with TTF derivatives. Vibrational spectroscopy data support a lack of significant charge transfer from the donor molecules to fullerene.[100] A distinctive feature of the molecular packing in such crystals is that the TTF derivatives forming the van der Waals contacts with adjacent fullerene molecules are non-planar (Fig. 7).

An analysis of structural data from the CSD regarding TTF-based molecular complexes (> 300 unique structures) shows that the molecules of TTF derivatives with bulky substituents or in the van der Waals crystals with large non-planar acceptors are often bent. Bending of the TTF moiety observed in almost all fullerene complexes with tetrachalcogenafulvalenes provides closer adjacency to a spheroidal C_n molecule and thus has purely van der Waals character (see Fig. 7). The complex $C_{60} \cdot (BEDT\text{-}TTF^+I_3^-)$ may be considered as an exception. It contains planar fulvalene as a radical cation.[101] Doping of the molecular complex $OMTTF \cdot C_{60} \cdot C_6H_6$ with alkali metals (K, Rb) gives rise to superconducting phases with relatively high temperatures of the transitions into the superconducting state T_c (17 K in the case of potassium and 23 K in the case of rubidium).[102]

Fused aromatic hydrocarbons and polyarenes, which are complementary to fullerenes in terms of the van der Waals shapes of their molecules, also form molecular complexes with fullerenes. Apart from the aforementioned buckminsterfullerene complex with 9,10-[9,10]anthracenoanthracene (DAN) $C_{60} \cdot DAN \cdot 3\,C_6H_6$,[92] the solvated complex with triptycene $C_{60} \cdot 2\,Trip \cdot 2\,(o\text{-}C_6H_4Me_2)$ may be taken as an example.[103] In many crystal structures, such polyarene derivatives adopt a conformation 'encompassing' the fullerene cage, thus increasing the number of energetically favourable van der Waals contacts.

The metal atoms in the coordination compounds with macrocyclic tetraazaligands (that form molecular complexes with fullerenes) have a square-planar coordination environment and thus are prone to additional coordination. In this class of compounds, zigzag chains of alternating fullerene and porphyrin molecules (Fig. 8) with shortened metal···fullerene contacts are frequently found. Such complexes are often regarded as supramolecular matrices capable of fixing a fullerene molecule in a specific orientation and therefore decreasing the rotational disorder of the crystal structure. In particular, the 'cage' molecule containing two zinc porphyrinate moieties linked in a way similar to that in paracyclophane strongly binds fullerene C_{60} in a complex with the composition 1 : 1, which is stable in solution. This complex has been isolated by chromatography[104] and studied by single-crystal X-ray diffraction.[105] Yet another complex, where one buckminsterfullerene molecule is embraced by two palladium porphyrinate units linked through a bridging group (Fig. 9), has also been characterised by single-crystal X-ray diffraction.[106] However,

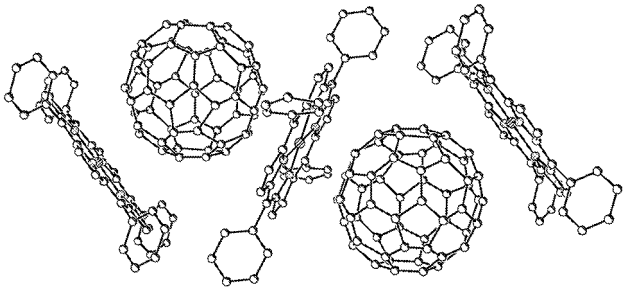


Figure 8. Zigzag chains in the crystal structures of fullerene complexes with metal porphyrinates.[47]

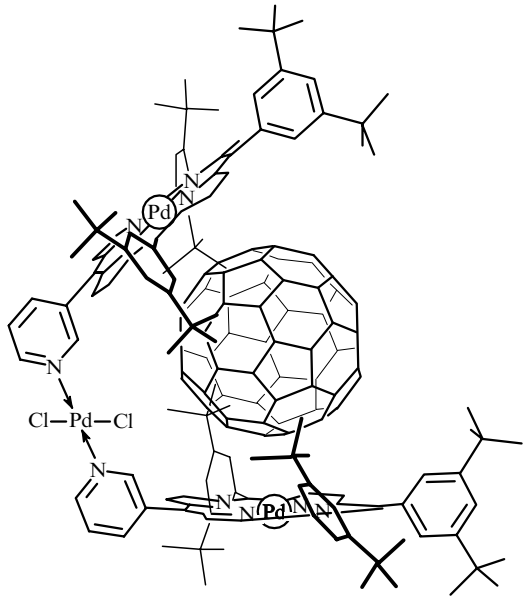


Figure 9. The molecular structure of a C_{60} complex with PdBPPyP containing two chemically bound Pd porphyrinate fragments.

both ordered and disordered fullerene molecules are revealed in the structurally characterised complexes with metal porphyrinates. Probably, the secondary metal···fullerene bonding is quite weak and does not exert decisive influence on the general molecular packing, though it can affect the degree of ordering of the fullerene molecules at specific favourable mutual arrangements of the porphyrin and fullerene molecules.[45]

The 'secondary' interactions of metalloporphyrins or related compounds with carbon cages, LM···C_n (L is a macrocyclic ligand), are characterised by the M···C distances intermediate between typical π-coordination (~2.0–2.3 Å) and van der Waals contacts (≥ 3.0 Å). For instance, the Fe···C distances are 2.70 Å in $C_{60}\cdot FeTPP^+\cdot(C_6F_5)_4B^-\cdot 2.5(o\text{-}C_6H_4Cl_2)$ complex.[107] In many cases, the secondary metal–fullerene interactions stabilise unique orientation of the fullerene cage preventing disorder. Nevertheless, in several substances of this class, for example, in the C_{60} complex with cobalt tetrakis(3,5-di-*tert*-butylphenyl)porphyrinate, both the short Co···C distances (2.59 Å) and disordering of the fullerene molecules are observed.[108]

Yet another class of fullerene molecular complexes includes cycloveratrylene and calixarenes. Some of these complexes contain molecules of water or alcohol in a crystal. This is quite nontypical for other classes of fullerene derivatives, which are most often hydrophobic. In the complexes with calixarenes, spheres of the fullerene molecules are laid on the bowl-shaped organic molecules. To date, sixteen different C_{60} complexes with substituted calixarenes starting from calix[3]- to calix[6]arenes have been characterised structurally (see Table 2). Water-soluble cyclodextrin also forms a complex with fullerene thus making it possible to transfer fullerene into an aqueous solution with a concentration of up to 10^{-5} mol litre^{-1}. The crystal structure of this complex has not been determined so far.[109]

Since the structural motifs $(C_n)_\infty$ in fullerene molecular complexes and chemically modified fullerenes are similar, it is convenient to analyse them in parallel. Figure 10 shows the numbers of all known crystalline fullerene derivatives as functions of the dilution parameter, MCN and the *R*-factor. The histogram of the dilution parameter distribution (see Fig. 10 *a*) manifests two maxima corresponding to $\rho = 0.8$ and 2.0. The former value is typical of layered hexagonal close packings and the latter, of loose framework structures. The values of $\rho \geqslant 3$, as a rule, correspond to chain or island motifs.

The distribution according to the MCN (see Fig. 10 *b*) of all fullerene structures deposited into the CSD indicates a large fraction of loose dilute structural motifs and a gradual decrease in the number of structures for the MCN ≥ 6. It is noteworthy that even molecular coordination numbers prevail over the odd ones, which may be explained by the frequent occurrence of the centrosymmetric motifs $(C_n)_\infty$.

The distribution according to the *R*-factor (see Fig. 10 *c*) is shifted to $R \geqslant 0.05$ and manifests a characteristic 'tail' at $R \geqslant 0.10$; the latter indicates a somewhat decreased accuracy of single-crystal X-ray diffraction for this specific class of crystalline compounds. Defects, stacking faults and very typical rotational disorder of spheroidal C_n clusters (dominated in the crystal structures with $R \geqslant 0.10$) are the reasons for the relatively low accuracy of the structure determination. For some fullerene

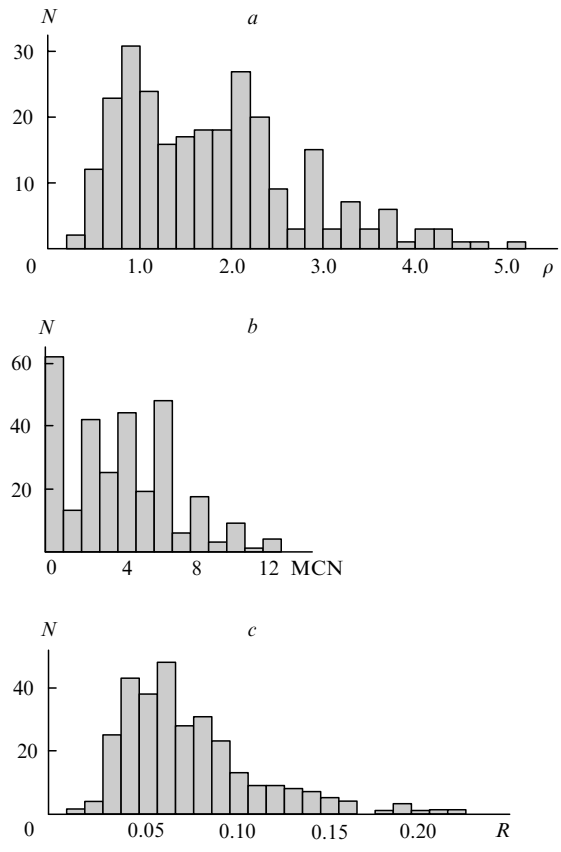


Figure 10. The number of fullerene structures from the CSD as a function of the dilution parameter (*a*), MCN (*b*) and *R*-factor (*c*).

molecular complexes, the 'guest' component is also disordered, which additionally reduces the quality of the crystallographic data.

In certain cases, it proves possible to approximate the rotational disorder of the fullerene molecules by superposition of C_n molecules in two orientations leading to coincidence of some of the atomic positions from the two orientations and partial occupancies of the remaining positions. In order to reduce correlations between fittable atomic positions in the least-squares refinement, a carbon cage with a fixed idealised geometry is often used. For C_{60}, two types of the rotational disorder occur most frequently (Fig. 11), *viz*., two orientations related to each other through a rotation by 90° around a molecular two-fold axis and two orientations related to each other through a rotation by 60° around a three-fold axis. In the former case, common positions determine 48 pairs of closely located carbon atoms from the two orientations, while the disordered part of the molecule (formed by spatially separated atomic positions with partial occupancies) forms characteristic 'crosses' at the vertices of an octahedron over the fullerene sphere. In the latter case, the disordered C_{60} molecule may be described as the ordered 'poles' and a disordered equatorial belt. For C_{70}, no similar regular superpositions of different molecular orientations have been revealed. Therefore, disordered structures are normally approximated by a superposition of two molecules with a fixed idealised geometry devoid of common atomic positions.

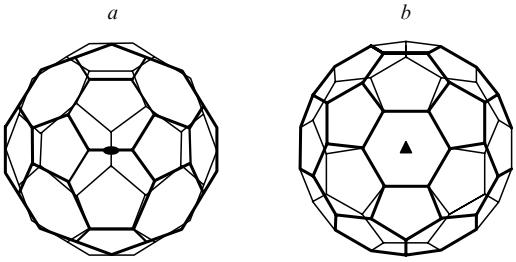


Figure 11. The major types of rotational disorder of the buckmisnterfullerene molecules in crystal structures (the two orientations are shown with bold and normal lines, respectively).
(*a*) rotation by 90° around the two-fold axis, (*b*) rotation by 60° around the three-fold axis.

To predict the preferred mutual orientations of rotationally disordered fullerene molecules, a model of the 'rubber cavity' has been proposed.[110] According to this model, all carbon atoms of the fullerene molecule residing in an equilibrium orientation occupy minima of the shallow van der Waals potential. To a first approximation, an increase in the interaction energy upon rotation of a molecule is proportional to the sum of squared radial stretches of the fullerene's van der Waals surface in the vicinity of atomic positions with respect to the initial equilibrium surface corresponding to the minimum interaction energy

$$\Delta U = k \sum \Delta r_i^2, \qquad (2)$$

where the summation is performed over radius-vectors of all carbon atoms. The most probable alternative orientations occurring in the case of a rotational disorder should correspond to the local minima of ΔU, *i.e*., to the least deformed van der Waals shape of molecule. A calculation based on the 'rubber cavity' model well reproduces both experimentally observed types of the rotational disorder for C_{60} as well as the lack of characteristic disorder types for C_{70}. Furthermore, this allows predictions of probable types of the rotational disorder for other highly symmetric spheroidal molecules (Fig. 12).

In some fullerene molecular complexes, as in pure fullerene, the second order phase transitions of the order–disorder type

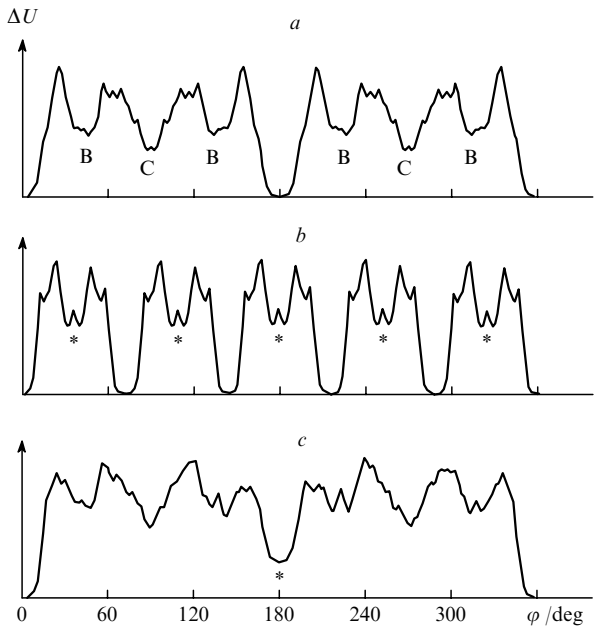


Figure 12. Profile of the interaction potential ΔU calculated within the model of the 'rubber cavity' for C_{60} (*a*), C_{80} (*b*) and $C_{60}F_{48}$ (*c*).
(*a*) Rotation by an angle φ around a two-fold axis; angles corresponding to the orientations giving rise to 'crosses' (C) and 'belt' (B) with partial occupancies of the atomic positions; (*b*) rotation by an angle φ around a five-fold axis; (*c*) rotation by an angle φ around a two-fold axis passing through the centres of two opposite 6/6 bonds; asterisks mark the second preferred orientations.

have been observed. For instance, such a phase transition takes place for the complex $C_{60} \cdot (C_6H_5)_2$ [111] where both the fullerene and biphenyl molecules are disordered. Upon a decrease in the temperature, two consecutive phase transitions occur resulting in the ordering of the two constituents: the biphenyl and fullerene molecules become ordered at 212 K and 147 K, respectively.

Fullerene-containing salts with bulky ions constitute a separate group, which is close to molecular complexes as regards their crystal chemistry. In such salts, fullerene may either be neutral [*e.g*., in $C_{60} \cdot$ BEDT-TTF$^+ \cdot I_3^-$ (see Ref. 110)] or charged [*e.g*., in $C_{60}^- \cdot 2\,Ph_4P^+ \cdot Cl^-$ (see Ref. 112)]. Both organic and metal-containing species can act as counterions. The latter can be exemplified by a series of isomorphous salts solvated by ammonia, *viz*., $C_{60}^{2-} \cdot M(NH_3)_6^{2+} \cdot 6\,NH_3$ [M = Mn, Cd (see Ref. 113), Co, Zn (see Ref. 114), Ni (see Ref. 115)]. These structures are built up of flat tetragonal layers of fulleride dianions and metal ammines with the octahedral coordination of the metals. Two other examples are the tetrahydrofuran solvate of potassium fulleride, $C_{60}^{3-} K_3^+ \cdot 14\,THF$ (see Ref. 116), and the toluene solvate of potassium 2,2,2-cryptand fulleride, $C_{60}^{2-} \cdot 2\,CryptK^+ \cdot 4\,PhMe$ (see Ref. 117) (both compounds are characterised by the island packing of the fullerene anions).

The properties of fulleride anions in the solid state and in solution have been recently reviewed.[118] As evidenced by cyclic voltammetry, buckminsterfullerene can undergo reversible reduction in solution yielding mono-, di- and trianions. Since the LUMO of fullerene is triply degenerate, the anions possess one, two and three unpaired electrons, respectively, and thus produce characteristic ESR spectra. Reduction of C_{60} to a diamagnetic hexaanion is possible in aprotic media.[119]

In this class of fullerene derivatives, as in molecular complexes, the structural motifs are determined primarily by van der Waals potential of the large C_n molecules. The packing of fulleride anions is somewhat denser than that in molecular complexes due to the electrostatic interactions with the cations. However, the

negative charge is evenly distributed over the fullerene molecule and does not prevent its rotation. Therefore, both ordered and disordered structures are found among anionic fullerene derivatives.

The low-temperature ferromagnetism has been observed for the fullerene radical-ionic salt with tetrakis(dimethylamino)ethylene, $C_{60}^{-} \cdot TDAE^{+}$, with the transition temperature of $T_c = 16$ K.[120] Some other analogous salts of buckminsterfullerene with donor amines (which have not been characterised structurally) also exhibit different types of ferromagnetic or antiferromagnetic ordering.[3] Attempts have been undertaken at the correlation of the magnetic properties of such compounds with rotation of the negatively charged fullerene cage.[121]

The fulleride anion carrying a negative charge from 1 – to 5 – is subject to Jahn – Teller distortions that result in deviations from the idealised I_h symmetry of the molecule. In the crystal structure of $C_{60}^{2-} \cdot 2(Ph_3P)_2N^{+}$, which has been determined with the highest accuracy, the completely ordered C_{60} molecule occupies the inversion centre.[122] The lengths of the 6/6 and 5/6 bonds lie in the ranges of 1.39 – 1.41 Å and 1.43 – 1.46 Å, respectively. The radial distortions of the carbon cage, calculated by us for this anion based on the atomic coordinates from the CSD, are shown in Fig. 13.

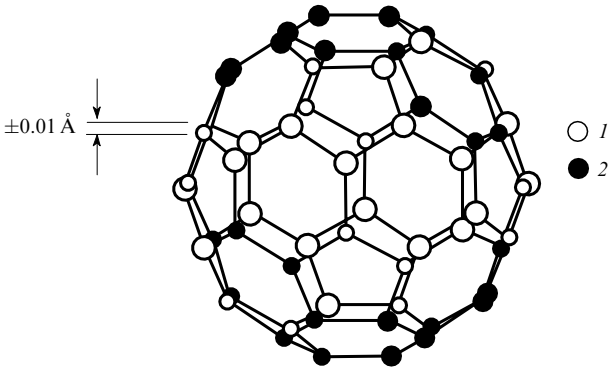


Figure 13. Radial Jahn – Teller distortions of the molecule C_{60} in the crystal structure of $C_{60}^{2-} \cdot 2(Ph_3P)_2N^{+}$ caclulated based on the atomic coordinates from the CSD.
(*1*) Atoms pushed out, (*2*) atoms pressed in. The magnitudes of the deviations from the idealised sphere are proportional to the radii of the circles (the scale is indicated).

Two ionic salts containing C_{60} dications, *viz*., $C_{60}(SbF_6)_2$ and $C_{60}(AsF_6)_2$, have been reported but not characterised structurally.[123] According to the ^{19}F NMR data, the hexafluoride anions therein freely rotate. Photoelectron spectra of the C_{60}^{+} ions in a molecular beam measured using SR have indicated dynamic Jahn – Teller disortions.[124]

V. Metal fullerides

The packing of carbon cages in ionic fullerene compounds with bulky inorganic or organic cations deviates from the close one and thus obeys the same regularities as in molecular complexes. In addition to these compounds, fullerene forms binary and ternary phases with metals that are similar to binary inorganic ionic salts. The majority of these phases have been characterised structurally using SR-based powder X-ray diffraction augmented with the Rietveld crystal structure refinement.

An interaction of solid buckminsterfullerene with alkali metals yields crystalline metal fullerides. A filling of, first, octahedral and then tetrahedral cavities in the fcc packing of the carbon spheres by alkali metal atoms gives rise to fullerides with stoichiometries MC_{60} and M_3C_{60}.[125, 126] Further doping results in substantial rearrangement of the whole structure. The final

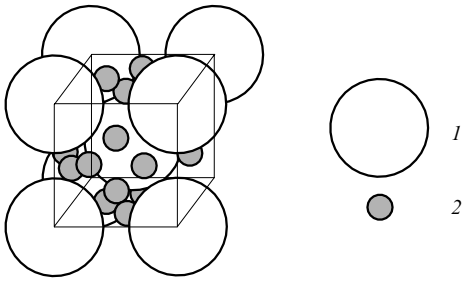


Figure 14. The crystal packing in metallofullerenes M_6C_{60}.
The unit cell is shown with thin lines; (*1*) C_{60}^{-}, (*2*) metal atom.

doping product is the M_6C_{60} phase[127] that is composed of the fullerene spheres forming a body-centred cubic packing and the squares of four metal cations situated in the centres of the faces of the cubic lattice (Fig. 14). An intermediate phase with the composition M_4C_{60} also exists. In its crystal structure, a part of the cavity is filled by 2 rather than 4 metal atoms so that the symmetry is lowered from cubic to orthorhombic.[128] Deeper doping is possible only in the case of lithium. It results in a product with the stoichiometry $C_{60}Li_{15}$, which is characterised by an fcc packing of the fullerene cages.[129]

Alkali metal fullerides containing buckminsterfullerene trianions (the LUMO of which is half-filled) are conductors at room temperature and transit into the superconducting state at low temperatures (18 K for K_3C_{60}).[130] As a result of systematic studies of phases with varied metallic component composition, a positive correltation between the critical temperature and the cubic lattice parameter has been established.[131] For the $Cs_xRb_{3-x}C_{60}$ salt, a value of $T_c = 33$ K has been obtained (see Ref. 132), while doping with a rubidium – thallium mixture has given rise to even higher temperature $T_c = 45$ K (see Ref. 133), which is the current record for fullerene derivatives. In a series of studies, Schön *et al.*[134] reported substantially higher critical temperatures achieved for the hole-doped fullerene and its solvates but these results were later disproved.[135] According to the calorimetric studies of M_3C_{60} salts, the orientational phase transition, typical of pure C_{60}, is also observed for them, but at higher temperatures (299 K for Na_2CsC_{60}, 313 K for Na_2RbC_{60} and 305 K for Na_2KC_{60}).[136]

The $KCsBaC_{60}$ and KBa_2C_{60} fullerides, which are characterised by similar structures but the higher charge of the fullerene anion, are relatively poor metallic-type conductors and do not manifest superconductivity.[137]

The fullerides containing the C_{60}^{6-} anions are dielectrics. A substitution of bications for a part of metal monocations resulting in an increase in the formal negative charge of the fullerene cage to nine (as in $K_3Ba_3C_{60}$), restores electroconductivity. A phase transition into the superconducting state has also been observed for the latter substance but at a lower temperature (5 K).[138] Fullerides of calcium Ca_5C_{60} (see Ref. 139) and barium Ba_6C_{60} (see Ref. 140) have crystal structures analogous to those of the M_6C_{60} salts (in the case of calcium derivative, one sixth of the metal atom sites remains vacant). They are conductors and show a supercondivity with the critical temperatures in the range of 4 – 8 K.

The crystal structure of ytterbium fulleride with the composition $Yb_{2.75}C_{60}$ can be described as an analogue of K_3C_{60}, in which 1/8 of all octahedral cavities is vacant, while the cations are shifted from the centres of the cavities. Due to ordering of the vacant sites, the lattice parameters of the original cubic cell are doubled and the lattice symmetry is lowered to orthorhombic.[141] Fullerides $M_{2.75}C_{60}$ similar to those discussed above and M_6C_{60} with a structure of K_6C_{60} have also been found in the systems C_{60} – Eu (see Ref. 142) and C_{60} – Sm (see Refs 143, 144). The orthorhombic phase $Sm_{2.75}C_{60}$ manifests an anomalous temperature dependence of the lattice constants (see Fig. 15): at $T < 32$ K, the thermal

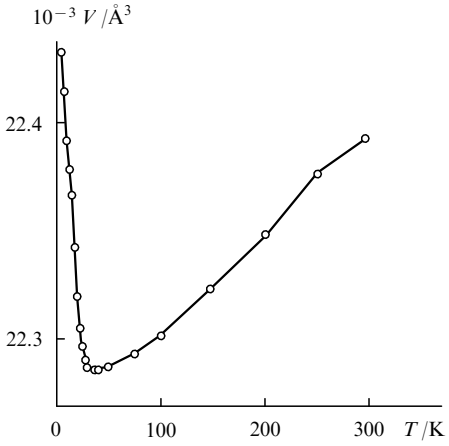


Figure 15. The temperature dependence of the unit cell volume for $Sm_{2.75}C_{60}$.[145]

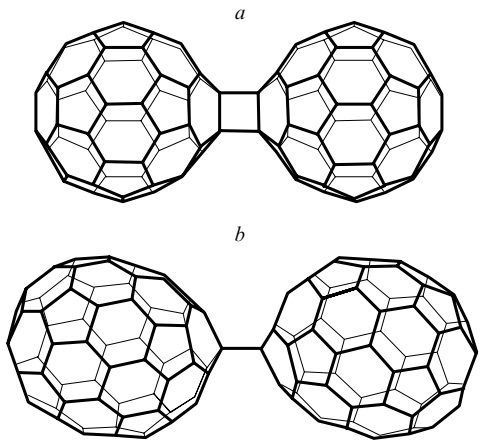


Figure 16. The molecular structures of the dimer $(C_{60})_2$ (*a*) [154] and dimeric anion $(C_{70}^-)_2$ (*b*).[155]

expansion coefficient becomes negative due to ordering of sites occupied by samarium di- and trications in the crystal lattice.[145]

With palladium and platinum, buckminsterfullerene forms crystalline compounds with the variable stoichiometry $C_{60}M_x$ ($1 \leqslant x \leqslant 7$) where formally zerovalent metal atoms are, probably, coordinated by double bonds of the fullerene molecules.[146, 147] This structural model has not been supported by diffraction techniques but it agrees well with the results of EXAFS on the palladium derivatives,[148] and gives a plausible explanation for the conversion of the palladium and platinum fullerides into the respective π-complexes with the η^2-C_{60} ligand upon action of organic phosphines PR_3.[6] The existing data on the structure of metallofullerenes have recently been surveyed by Ivanova.[149]

The C_{70} fullerene forms a series of fullerides with alkali metals characterised by stoichiometries MC_{70}, M_4C_{70} and M_6C_{70}.[150] The M_3C_{70} phase with an fcc lattice is stable only at elevated temperatures and readily converts upon cooling into the trigonal phase or disproportionates. Nevertheless, it can be stabilised by a proper selection of cations with suitable sizes (*e.g.*, sodium and caesium in Na_2CsC_{70}) so that the two smaller sodium cations occupy the tetrahedral cavities while the larger caesium cation is in the octahedral cavity.[151] An fcc phase with the composition Ba_3C_{70} has also been prepared.[152] Since the LUMO of the C_{70} molecule is nondegenerate and the next-in-energy orbital is doubly degenerate (see Fig. 3), the HOMO of the C_{70}^{4-} anion is half-filled. Respectively, salts M_4C_{70}, like M_3C_{60}, manifest superconductivity. A series of rare earth metal [70]-fullerides have also been described. In particular, two europium fullerides with stoichiometries $Eu_{3-x}C_{70}$ and $Eu_{9-x}C_{70}$ have been isolated.[48] According to powder X-ray diffraction, the former phase is antiferromagnetic and has a monoclinic structure, which is similar to $M_{2.75}C_{60}$ in the arrangement of the guest atoms. The latter phase is ferromagnetic and similar in structure to face-centred cubic M_6C_{60} fullerides. However, in the europium derivative, small metal clusters rather than single atoms occupy the octahedral cavities.[48]

Fullerides of higher fullerenes are less explored. The final product of doping of C_{84} with potassium is the salt $K_{8+x}C_{84}$, which is structurally similar to K_6C_{60} and contains fully ordered fullerene anions. Yet another fulleride, K_3C_{84}, is characterised by a rotational disorder of fullerene molecules and a lower metal content due to partial occupancies of potassium sites.[153]

VI. Fullerene-based oligo- and polymers

Due to the presence of double bonds, fullerenes form oligo- and polymers upon irradiation, under pressure, upon heating or action of chemical anionic or radical initiators. Transformations of fullerenes at elevated pressures have recently been reviewed.[5]

Pure buckminsterfullerene forms dimers under conditions of anionic catalysis.[154] According to the single-crystal X-ray diffraction studies of the dimer C_{120} solvate with *o*-dichlorobenzene, the dimerisation proceeds as a [2 + 2] cycloaddition at the 6/6 bond (Fig. 16 *a*). In the four-membered ring composed of the sp^3-hybridised carbon atoms (the corresponding spherical excesses are 26.2 – 26.7°), the C – C bond lengths are 1.581 Å and 1.575 Å for the 6/6 bonds within the fullerene core and exopolyhedral bonds, respectively. Synthesis of the C_{60} dimer from the molecular complex $(BEDT\text{-}TTF)_2C_{60}$ in which the 6/6 bonds of the adjacent fullerene molecules are mutually oriented to each other at a pressure of 5 GPa has been described.[156] Several isomeric C_{60} trimers have been produced as evidenced by mass spectrometry and high-resolution electron microscopy; however, these species have not been isolated as individual substances.[157]

A cross-dimer of C_{60} and C_{70} with an unknown structure has been prepared by means of mechanochemistry.[158] According to the quantum chemistry calculations, this may represent a [2 + 2] cycloaddition product to the C_{70} moiety at the *b*-type 6/6 bond (see Fig. 1 *b*).

Buckminsterfullerene forms several polymer phases at elevated pressures. Some of them have been obtained as single crystals and studied by single-crystal X-ray diffraction. At early stages of the modification, the phase contains linear polymeric chains of fullerene cores and is characterised by an orthorhombic lattice.[159] A deeper modification at a pressure of 2 – 5 GPa yields rhombohedral [160] and tetragonal [161] phases composed of hexagonal and tetragonal layers of covalently bound C_{60}, respectively. A detailed single-crystal X-ray diffraction study of the tetragonal phase [162] has revealed that it is rather orthorhombic with a tetragonal pseudosymmetry ($a \approx b$), though in another work, the lattice has been interpreted as being tetragonal.[163] The interfullerene C – C bond in the polymer is 1.60 Å. According to the powder X-ray diffraction, polymerisation at higher pressures (13 GPa) results in a quite irregular three-dimensional network of bound fullerenes.[164] Polymerisation of C_{60} and C_{70} at a pressure of 8 GPa and 800 – 900 °C is accompanied by partial destruction of the carbon clusters and formation of amorphous carbon materials. Densities of some of these materials were reported to approach that of diamond.[164, 165]

Polymerisation of fullerene anions occurs more easily. In particular, a linear polymer is formed from the cubic fulleride Na_2CsC_{60} at 0.7 GPa.[166] Alkali metal fullerides with the stoichiometry MC_{60}, in which fullerene anions are rotationally disordered at room temperature, form polymers with the C_{60} units joined into infinite chains by single C – C bonds upon lowering tempertures.[167] The radical-ionic salt $Cp'_2Cr \cdot C_{60} \cdot 2C_6H_4Cl_2$ ($Cp' = C_5Me_5$) at room temperature contains the $(C_{60})_2^{2-}$ dimers

linked by one C–C bond with a length of 1.60 Å.[168] Another radical-ionic salt, $(C_6H_5Me)_2Cr^+ \cdot C_{60}^- \cdot CS_2$, represents, according to single-crystal X-ray diffraction data, a linear polymer with unusually short non-bonding intermolecular C–C contacts of 2.24 Å.[169] In the $(C_6H_5Me)_2Cr-C_{60}$ system, a solvent-free molecular complex with the composition 1 : 1 has been found, in which C_{60} clusters exist as independent rotationally disordered anions at high temperatures (> 250 K) and as dimeric dianions bound by one σ-bond at low temperatures.[170]

The C_{70} fullerene also undergoes polymerisation both as a neutral molecule and an anion. The crystal structure of a polymer prepared from pure hexagonal C_{70} (a calculation within the atom–atom potential approach has shown that the mutual orientation of the molecules in cubic C_{70} is unfavourable for a formation of polymeric chains) has been determined.[171] In the polymer, the C_{70} molecules are joined in chains as a result of a [2 + 2] cycloaddition at the *b*-type 6/6 bonds (see Fig. 1 *b*). In the dimethylformamide–benzene solvate of a molecular complex of the radical-ion salt $Cs_2(C_{70})_2 \cdot CTV \cdot (DMF)_5 \cdot C_6H_6$ with cycloveratrylene (see Table 2), the fulleride anion exists as a dimer $(C_{70}^-)_2$. Two fullerene moieties are linked through one bond with the length of 1.56–1.58 Å (for different symmetrically independent dimers) involving the type **1** carbon atoms (see Fig. 1 *b*). The C_{70} core is non-symmetrically distorted so that the pentagonal 'pole' of the molecule acquires an envelope conformation with the C(sp^3) atom at the top point (Fig. 16 *b*).[155] In ammonia-solvated fullerides $MC_{70} \cdot n\,NH_3$ (M = Ca, Sr, Ba, Eu, Yb), the C_{70}^{2-} anions are bound into infinite chains by the exopolyhedral C–C bonds.[172]

VII. 'Binary' compound

In terms of chemical reactivity, fullerenes are similar to conjugated polyalkenes. The stable fullerene core may be considered as a large pseudoatom in reactions of addition and substitution involving exopolyhedral fragments. In this section, fullerene 'binary' compounds C_nX_m where X is an external atom or a stable substituent (CH_3, CF_3) covalently bound to the fullerene core C_n are discussed.

Structural studies of polyadduct mixtures C_nX_m are hindered by the multitude of addition isomers. For instance, a symmetrical addition of two functional groups to one of the 30 equivalent 6/6 bonds in buckminsterfullerene divides the remaining 6/6 bonds into nine nonequivalent classes. The number of theoretically possible isomers increases tremendously with an increase in the number of groups attached (*e.g.*, 6×10^{14} for $C_{60}H_{36}$, see Ref. 173), which makes impossible a comprehensive quantum chemistry analysis with a search for the global minimum.

Upon exposure of buckminsterfullerene to air, traces of C_{60} oxides are formed. For purposeful preparation of oxides, *m*-chloroperoxybenzoic acid is used, which is a standard reagent for the oxidation of alkenes into epoxides. Monoxide $C_{60}O$ (see Ref. 174) and dioxide $C_{60}O_2$ (see Ref. 175), which have been isolated and characterised structurally, form single crystals isomorphous to pure buckminsterfullerene. Exopolyhedral oxygen atoms occupying cavities of the fcc packing have not been revealed due to rotational disorder. For the $C_{60}O$ oxide, an orientational phase transition has been registered at 278 K. According to the single-crystal X-ray diffraction study of oxyfullerene π-complexes, the oxygen atom in $(\eta^2\text{-}C_{60}O)Ir(CO)Cl(PPh_3)_2$ is attached to the 6/6 bond of the fullerene cage while the iridium atom is coordinated to another 6/6 bond of the same hexagon.[176] In the $C_{60}O_2$ core of another complex, *viz.*, $(\eta^2\text{-}C_{60}O_2)Ir(CO)Cl(PPh_3)_2$, two oxygen atoms are attached to neighbouring 6/6 bonds; the complex represents a mixture of isomers with metal atoms coordinated to different 6/6 bonds.[177] In the $C_{70}O$ core of the complex $(\eta^2\text{-}C_{70}O)Ir(CO)Cl(PPh_3)_2$,[178] the oxygen and iridium atoms are attached to adjacent *b*-type 6/6 bonds (see Fig. 1 *b*).

The properties of fullerene hydrides have been reviewed by Goldshleger and Moravsky.[4] The principal buckminsterfullerene hydrogenation product is $C_{60}H_{36}$, which was suggested to be a mixture of D_{3d} and S_6 isomers based on the data from IR and Raman spectroscopy.[179] Meanwhile, a fullerene hydride with the same composition was attributed[180] to a mixture of two other isomers with the C_3 and C_1 symmetry (isostructural to isomers of fullerene fluoride $C_{60}F_{36}$, see below) using the ^1H, ^{13}C and ^3He NMR data for the endohedral derivative $He@C_{60}H_{36}$. Another hydride, $C_{60}H_{18}$, was also suggested to be isostructural to the respective fluoride[181] based on the ^3He NMR data for $^3He@C_{60}X_{18}$ (X = H, F).[182] To our knowledge, no single-crystal X-ray difraction studies of fullerene hydrides have been conducted so far. In a study of $C_{60}H_{36}$ using powder X-ray diffraction, a bcc lattice with a lattice parameter of 11.75 Å was determined.[183]

Iodine forms no covalent compounds with C_{60} but rather a molecular complex $C_{60} \cdot 2I_2$ belonging to a structural type with closely packed hexagonal layers $(C_{60})_\infty$.[184] An iodine-containing solvate $C_{60} \cdot PhMe \cdot I_2$ falling into the same type of molecular packing has also been characterised.[185] All other halogens react with fullerenes to form addition products.

A series of fluorinated buckminsterfullerenes from $C_{60}F_2$ (see Ref. 186) to $C_{60}F_{48}$ (see Ref. 187), in which the polyhedral C_{60} core is retained, have been prepared and characterised. The methods of synthesis of fluorofullerenes and reported data on their structures have been recently reviewed by Taylor.[188] To date, single-crystal X-ray diffraction data are available for $C_{60}F_{18}$ (see Refs 189, 190), $C_{60}F_{18}O$ (see Ref. 191), $C_{60}F_{17}CF_3$ (see Ref. 192), $C_{60}F_{36}$ (three isomers)[193, 194] and $C_{60}F_{48}$ (see Refs 195, 196). The Schlegel diagrams for the structurally studied fullerene fluorides and bromides are given in Fig. 17. The molecular structures of three C_{60} fluorides are shown in Fig. 18, and their basic geometrical parameters are listed in Table 5.

In the molecule $C_{60}F_{18}$ with the C_{3v} symmetry studied as a toluene solvate[189] and individual fullerene fluoride,[190] all eighteen fluorine atoms are attached to one hemisphere of the fullerene core around a flattened hexagonal ring (the spherical excess is $\varphi_i \leqslant 0.1^\circ$) isolated from the π-system of the remaining part of the molecule (see Fig. 17 *a*). All the sp^3-hybridised carbon atoms are pyramidised ($26.4^\circ \leqslant \varphi_i \leqslant 29.9^\circ$) while the atoms adjacent to them are flattened ($\varphi_i = 3–6^\circ$) with respect to pristine C_{60}. Consequently, the carbon cage acquires the shape of a 'tortoise shell' (see Fig. 18 *a*).

Table 5. Parameters of the molecular geometry of structurally characterised fluorofullerenes.

Formula	Symmetry	C–C bonds /Å				k [a]	*R*-factor	Disorder	Ref.
		$sp^3–sp^3$	$sp^3–sp^2$	aromatic	C=C				
$C_{60}F_{18} \cdot PhMe$	C_{3v}	1.54–1.67	1.47–1.53	1.37	–	0.74	0.049	no	189
$C_{60}F_{36} \cdot 1.75\,PhMe$	T	1.55–1.66	1.48–1.49	1.36–1.38	–	0.70	0.090	yes	193
$C_{60}F_{36} \cdot 3.5\,PhMe$	C_1	1.54–1.68	1.46–1.54	1.37–1.38	1.32	0.70	0.059	no	194
$C_{60}F_{48} \cdot C_6H_3Me_3$-1,3,5	S_6	1.54–1.61	1.49–1.58	–	1.29–1.30	0.71	0.051	yes	195

[a] k is the Kitaygorodsky molecular packing coefficient.[64]

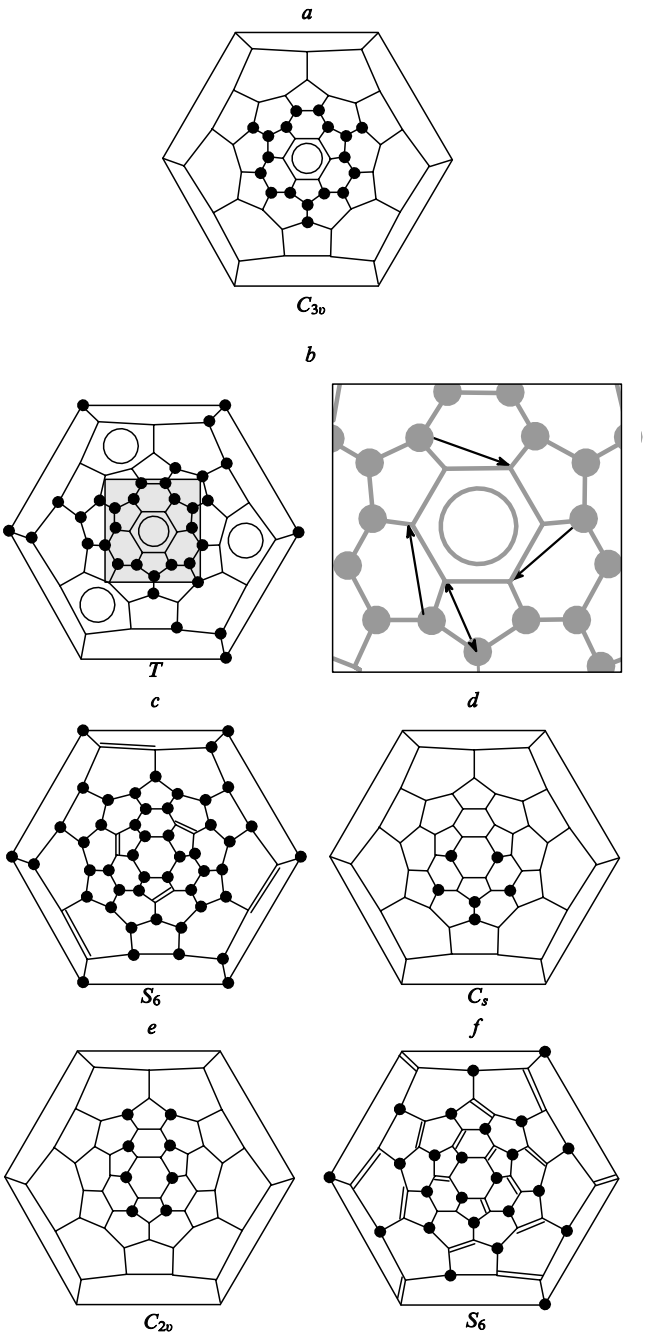


Figure 17. The Schlegel diagrams for $C_{60}F_{18}$ (*a*), $C_{60}F_{36}$ (*b*), $C_{60}F_{48}$ (*c*), $C_{60}Br_6$ (*d*), $C_{60}Br_8$ (*e*), $C_{60}Br_{24}$ (*f*); (*b*) (to the right): the arrows show the 1,3-shifts of fluorine atoms giving rise to the C_3 isomer, the double arrow shows the shift transforming the C_3 isomer further to the C_1 isomer; (*a*, *b*): aromatic rings are shown; (*c*, *f*): positions of double bonds are shown.

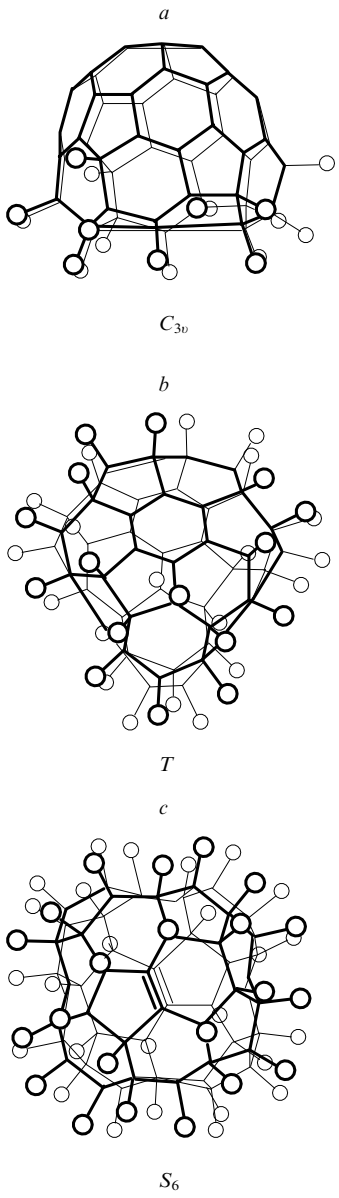


Figure 18. The molecular structures of $C_{60}F_{18}$ (*a*), $C_{60}F_{36}$ (*b*) and $C_{60}F_{48}$ (*c*).

Three symmetrically equivalent 5/6 $C(sp^3)-C(sp^3)$ single bonds in the molecule $C_{60}F_{18}$ are elongated to 1.67 Å. The addition of an oxygen atom at one of these bonds (to give $C_{60}F_{18}O$) results in its cleavage.[191] Three fluorine atoms the most remote from the isolated aromatic hexagon can be substituted by phenyl groups (using the Friedel – Crafts reaction) to give $C_{60}F_{15}Ph_3$ [197] and undergo nucleophilic substitution.[198] In the crystal structure of $C_{60}F_{17}CF_3$, the trifluoromethyl group occupies one of the peripheral fluorine sites; the crystal contains a mixture of two substitution isomers in different orientations.[192]

The molecular structure of the fluoride $C_{60}F_{20}$ (not studied by single-crystal X-ray diffraction) has been determined by NMR spectroscopy. According to Boltalina *et al.*,[199] all fluorine atoms in $C_{60}F_{20}$ are located at the equatorial belt of the molecule, *i.e.*, this fluoride does not include a fragment of the $C_{60}F_{18}$ structure. This suggests that, under the reaction conditions, the fluorine atoms migrate over the surface of C_{60}.

Several isomers of $C_{60}F_{36}$ are known. The major isomer with the exceptionally rare point symmetry *T* has been isolated and structurally characterised as a toluene solvate. This molecule contains four aromatic rings with equal bond lengths analogous to the single aromatic ring in $C_{60}F_{18}$. All other carbon atoms are sp^3-hybridised and bound to fluorine atoms. The strongly distorted carbon core acquires a shape resembling a tetrahedron with rounded edges and vertices (see Fig. 18 *b*). The crystal is statistically disordered and represents a racemic mixture of enantiomers.[194] The C_3 symmetry has been attributed to the isomer second in abundance based on the NMR data. The third isomer having the C_1 symmetry has been isolated and studied by single-crystal X-ray diffraction. Its molecular structure can be derived from that of the C_3 isomer by a 1,3-shift of one of the fluorine atoms in the five-membered ring [194] (see Fig. 17 *b*).

The fluorine-rich fullerene fluoride, $C_{60}F_{48}$, has been characterised by single-crystal X-ray diffraction as a solvate with mesitylene.[195, 196] The molecule occupies a special position of the $\bar{3}$ symmetry in a pseudocentred cubic lattice (space group $Pa\bar{3}$) and is rotationally disordered. It can be interpreted as a superposition of the D_{3d} and S_6 isomers in an overall ratio of 0.61 : 0.39.[195] In another study,[196] the unit cell was erroneously attributed to a bcc lattice and the molecule $C_{60}F_{48}$ was described as an S_6 isomer.

The $C(sp^3)-C(sp^3)$ bond lengths in $C_{60}F_{48}$ lie in the range 1.54 – 1.61 Å.[195] Six double carbon – carbon bonds (1.29 – 1.30 Å) situated at vertices of an octahedron (see Fig. 17 *c*), which belong to the 5/6 type (in contrast to respective bonds in the pristine fullerene), are noticeably pressed inside the molecule (the spherical excesses are from -2° to -9°).‡ This is consistent with the impossibility of further fluorination of C_{60} derivatives without disruption of the carbon cage.[200]

Due to the strong electrostatic dipole – dipole interactions (the dipole moment is 12 – 15 D, according to *ab initio* quantum chemistry calculations), both components of the $C_{60}F_{18}\cdot PhMe$ solvate are ordered. The Kitaygorodsky density coefficient[64] of the molecular packing for $C_{60}F_{18}\cdot PhMe$ is 0.74 (the packing of pure $C_{60}F_{18}$ is significantly looser since the lattice cavities cannot be filled with the solvent molecules). Meanwhile, solvates of the high-symmetry fluorides $C_{60}F_{36}$ and $C_{60}F_{48}$, which are characterised by zero dipole moments, are looser and more disordered ($k = 0.70 – 0.71$, see Table 5). The pattern of the rotational disorder of the molecules $C_{60}F_{48}$ observed in the crystal structure of $C_{60}F_{48}\cdot 2(1,3,5\text{-}C_6H_3Me_3)$[196] can be reproduced within the model of the 'rubber cavity'[110] (see Fig. 12).

Chlorination of fullerene yields a mixture of products $C_{60}Cl_n$, $n \leqslant 24$. These products have been studied by IR spectroscopy and mass spectrometry.[201] Using a mild chlorinating agent (ICl), the chloride $C_{60}Cl_6$ can be prepared. According to the NMR and IR data, its structure is similar to that of hexabromide (see Fig. 17 *d*).[202]

Six exopolyhedral fragments in hexamethylfullerene $C_{60}Me_6$ produced by methylation of $C_{60}Cl_6$ with methyllithium are arranged in the same mode as in hexachloride according to its single-crystal X-ray diffraction study.[203] Partial substitution of the methyl groups for the chlorine atoms to give $C_{60}Me_5Cl$ followed by a nucleophilic substitution of OH for Cl and epoxidation of the two C – C bonds in the isolated five-membered ring yields $C_{60}Me_5(OH)O_2$, the crystal structure of which has also been determined.[204] In this structure, the molecules are ordered and characterised by the C – C bond lengths of 1.52 – 1.57 Å for the $C(sp^3)-C(sp^3)$ bonds and 1.48 Å for the epoxy-rings. The C – O bond lengths lie in the range 1.44 – 1.46 Å. Five chlorine atoms around a five-membered ring in $C_{60}Cl_6$ can also be substituted by phenyl groups using the Friedel – Crafts reaction (in this reaction, $C_{60}Ph_4$ is produced as a by-product).[205] The electronic properties of the main product $C_{60}Ph_5Cl$ are similar to pentasubstituted cyclopentadiene. In particular, its two-electron electrochemical reduction gives rise to an aromatic anion,[206] and its chemical modification enables preparation of metal π-complexes of the η^5 type.

Nakamura *et al.*[50] isolated and studied structurally a fullerene derivative functionalised in a similar way at two opposite pentagonal faces. The equiatorial belt of such a fullerene cage is composed of sp^2-hybridised carbon atoms resembling a fragment of a [5,5]-nanotube (Fig. 19). Trifluoromethylation of C_{60} using silver trifluoroacetate on heating yields CF_3 addition products to the neighbouring 6/6 and 5/6 bonds, according to the NMR data.[207]

Single-crystal X-ray diffraction data for three buckminsterfullerene bromides $C_{60}Br_6$, $C_{60}Br_8$ and $C_{60}Br_{24}$ crystallised as solvates with liquid bromine have been published (the respective Schlegel diagrams are shown in Fig. 17 *b*). In the two latter molecules, the nearest bromine atoms occupy 1,3-positions to each other, which is, probably caused by steric reasons. In the molecule $C_{60}Br_{24}$, there are isolated double bonds belonging both to the 5/6 and 6/6 types. They are shortened to 1.33 – 1.34 Å, while the $C(sp^2)-C(sp^3)$ bonds are elongated to 1.46 – 1.51 Å. The packing of the molecules $C_{60}Br_{24}$ in the crystal lattice is close to fcc.

‡ Negative spherical excesses correspond to a pyramidal carbon atom with an apex directed towards the centre of the fullerene cage.

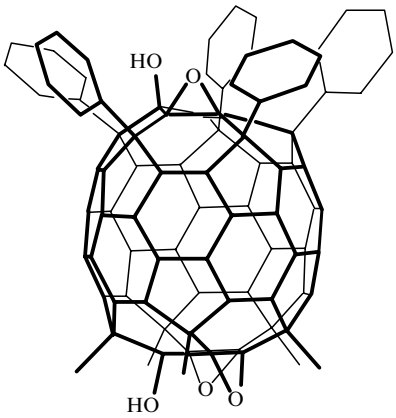


Figure 19. The molecular structure of $C_{60}Me_5Ph_5O_3(OH)_2$ with the fullerene core functionalised at two opposite pentagonal faces.[49]

Binary derivatives of C_{70} are less studied. The major hydrogenation products fall into the composition range $C_{70}H_{36} – C_{70}H_{44}$ (see Ref. 4). The fluorine-rich derivative is, likely, $C_{70}F_{56}$,[208] while chlorination stops at the $C_{70}Cl_{10}$ stage.[209] Substitution of methyl groups for chlorine atoms in this chloride is accompanied by partial reduction and yields $C_{70}Me_8$. The crystal structure of this substance has been determined.[210] The Me-fragments are attached to the type **4** carbon atoms (see Fig. 1 *b*) at both sides with respect to the equator of the molecule. In the bromide $C_{70}Br_{10}$, which has been also studied by single-crystal X-ray diffraction (Fig. 20), the bromine atoms are attached to the type **4** carbon atoms as well.[49] Synthesis of another bromide $C_{70}Br_{14}$ has been reported,[211] but its crystal structure has not been determined. Among binary derivatives of higher fullerenes, only one bromide $C_{78}Br_{18}$ has been studied, which contains statistically disordered molecules of two bromination isomers with the C_{2v} symmetry; no admixtures of probable bromination products of the D_3 isomer were detected.[212]

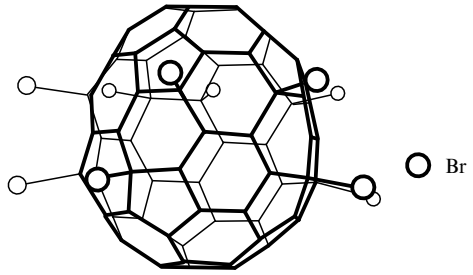


Figure 20. The molecular structure of $C_{70}Br_{10}$ from the single-crystal X-ray diffraction data.[49]

VIII. σ-Derivatives

Derivatisation of fullerene typically involves an addition to the 6/6 double C – C bond as the first stage. Thus, exocoordinated carbon atoms acquire the sp^3-character and protrude over the surface of the original C_{60} sphere due to an elongation of the C – C bond

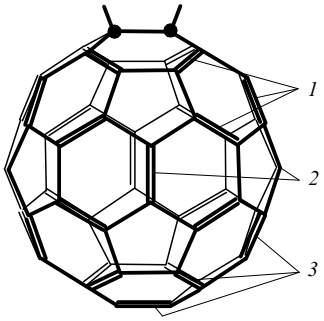


Figure 21. Symmetrically non-equivalent 6/6 bonds in the molecule C_{60} chemically modified at one of the 6/6 bonds.
Positions of bonds: (*1*) *cis*, (*2*) equatorial, (*3*) *trans*.

linking them and an increase in the spherical excesses φ_i from 12° to 16–32° ($\varphi = 31.7°$ for an unstrained sp^3-hybridised carbon atom). Such an addition to one of the 6/6 bonds divides the remaining 6/6 bonds in the fullerene molecule into 9 symmetrically nonequivalent types. Three of these types are conventionally referred to as *cis*-positions, four — *trans*-positions and two — equatorial positions (Fig. 21).

The main types of the σ-addition products to the molecule C_{60} are shown in Fig. 22. The binary products $C_{60}X_n$ produced by multiple σ-addition of one-electron fragments X to C_{60} were discussed in the previous section.

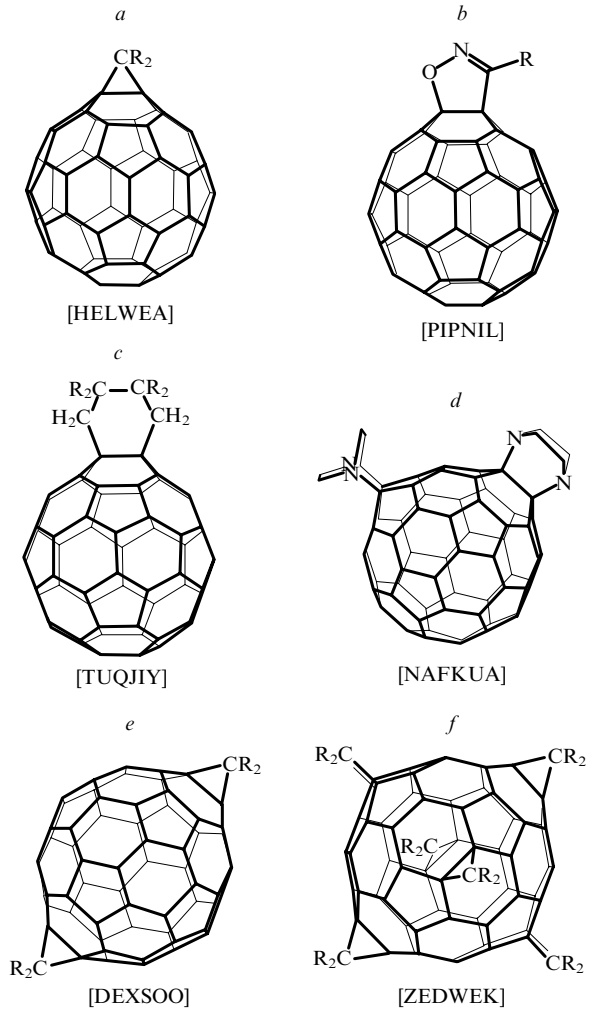


Figure 22. The possible types of σ-functionalisation of the fullerene molecule (CSD Refcodes are given).

The addition of carbene to a double carbon–carbon bond within the fullerene molecule yields a three-membered ring (see Fig. 22 *a*,*e*,*f*). On average, the key $C(sp^3)-C(sp^3)$ bond in these compounds is elongated to 1.59 Å, which is 0.04–0.05 Å longer than a typical single C–C bond. This clearly indicates substantial steric strains around the sp^3-hybridised carbon atoms in the fullerene core. Four-membered rings have been found only in derivatives of the dimeric molecule $(C_{60})_2$. Numerous derivatives with five- and six-membered rings (see Fig. 22 *b*–*d*) are formed in the reactions of [2 + 3] and [2 + 4] cycloaddition. As a result, the mean length of the C–C bond involved in the attachment increases to 1.60 Å and 1.61 Å, respectively.

Functionalisation of a double bond activates the five other 6/6 bonds, which form together an octahedron over the C_{60} core (see Fig. 22 *d*,*e*), towards further addition. Subsequent addition proceeds predominantly at these bonds giving rise ultimately to a hexaadduct with the T_h symmetry of the carbon cage (see Fig. 22 *f*). For instance, the crystal structure of the adduct containing six malonate groups $C_{60}[C(COOEt)_2]_6$ has been determined.[213] However, a hexaaduct violating this addition pattern is known, which is characterised by the composition $C_{60}(Tmp)_6 \cdot Solv$ and D_3 symmetry.[214]

Homofullerenes (*i.e.*, the addition products to the 5/6 bonds) are less abundant. Formally, this bond is single, and the attachment to it results in its cleavage and removal of the two carbon atoms to a distance ~2.1 Å from each other.[191,215]

The fullerene C_{70} possesses 8 non-eqivalent C–C bonds, which are characterised by different steric accessibilities. In the majority of structurally characterised derivatives, the addition occurs at the *b* type double bond (see Fig. 1 *b*), which is characterised by the largest sum of spherical excesses of its two carbon atoms among all the 6/6 bonds. Two exceptions to this rule are the adduct $C_{70}C_{10}H_{12}O_2$ [216] in which the *d* type bond is affected and a homofullerene produced by the addition of CCl_2 to the *f* type single bond, which results in its cleavage.[215]

Crystal packing of certain functionalised fullerenes is affected to a great extent by the external groups attached to the C_{60} or C_{70} core (which, for instance, link two fullerene cores or coordinate metal atoms). In particular, OsO_4, which is often used in organic synthesis for oxidation of alkenes to diols, reacts with buckminsterfullerene yielding an osmate ester of fulleren-1,2-ol. Note that the complex $C_{60}O_2OsO_2(4\text{-}BuPy)_2$ is the very first C_{60} derivative studied by single-crystal X-ray diffraction.[217] There are several other complexes, in which metal atoms are coordinated to exopolyhedral fragments attached to a fullerene core. As an example, a solvate of $C_{60}S_2Fe_2(CO)_6$ may be mentioned, in which two sulfur atoms attached to the fullerene core in 1,2-positions additionally coordinate the binuclear $Fe_2(CO)_6$ fragment.[218]

In addition to the aforementioned fullerene dimer, there are other molecules containing two fullerene cages bound to each other. Some typical examples are given in Fig. 23. Oxybifullerene $C_{120}O$ (its radical cation $C_{120}O^+$ is readily formed upon oxidation of solutions of C_{60} in air giving rise to a characteristic ESR signal, see Ref. 118) has been characterised by single-crystal X-ray diffraction as a molecular complex with octaethylporphyrin. Despite the positional disorder of the oxygen atoms, it was established that the molecule represents a dimer, in which one of the interfullerene C–C bonds is replaced by the C–O–C bridge.[82] In $C_{60}C(C{\equiv}CSiPr^i_3){-}C{\equiv}CC{\equiv}C(C{\equiv}CSiPr^i_3)CC_{60}$ (see Fig. 23 *a*), two 1,2-disubstituted fullerene cores are linked by a four-atomic butadiynediyl bridge.[219] A derivative of the dimer C_{60} where each of the fullerene cages is additionally functionalised at five bonds giving the addition pattern similar to C_{60} hexaadducts has been studied (see Fig. 23 *b*).[220] Yet another metallocomplex involving two fullerene fragments functionalised to hexaadducts and acting as bidentate σ-ligands has been synthesised and structurally characterised. The fullerene fragments in this complex

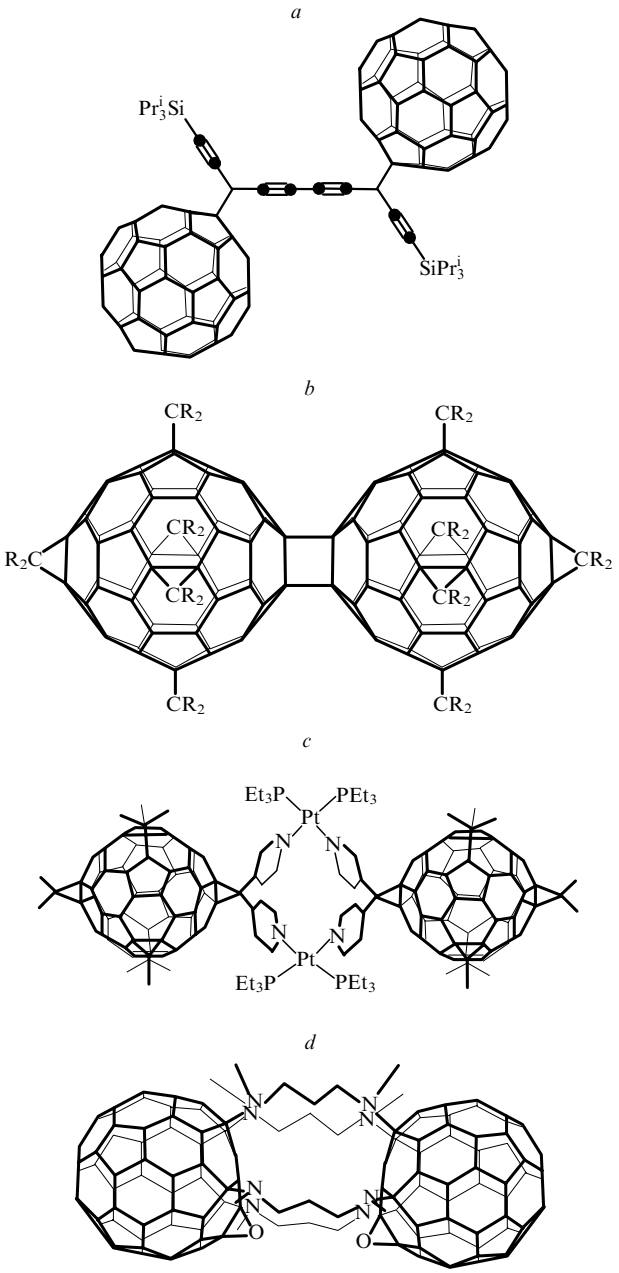


Figure 23. The structures of molecules containing two C_{60} moieties; (*a*) 1,4-bis{(1,2-dihydro-61-[(triisopropylsilyl)ethynyl]-1,2-methano-C_{60}-fullerene-61-yl}buta-1,3-diyne,[219] (*b*) bis[decakis(ethoxycarbonyl)pentacyclopropa(1,9 : 16,17 : 44,45 : 52,60)-C_{60}-fullerenediyl],[220] (*c*) bis{[μ^2-66,66-bis(4-pyridyl)-1,2 : 18,36 : 22,23 : 27,45 : 31,32 : 55,56-hexakis(methano)-C_{60}-fullerene-61,61,62,62,63,63,64,64,65,65-decakis(ethylcarbonate)-*N*,*N*′] bis(triphenylphosphino) platinum(II)},[221] (*d*) tetrakis(*N*,*N*′-dimethylpropanediamine-*N*,*N*′)bis(epoxy-C_{60}-fullerene).[222]

are linked by two bridging platinum atoms (see Fig. 23 *c*).[221] In 2000, the first fullerene-containing cryptand $(C_{60}O)_2 \cdot [NMe(CH_2)_3NMe]_4$ was synthesised, which may be regarded as a derivative of fullerene hexachloride, in which two chlorine atoms are substituted by an epoxy oxygen atom, while the other four atoms are substituted by propanediamine bridges joining two $C_{60}O$ moieties (see Fig. 23 *d*).[222]

The changes in the C–C bond lengths in the C_{60} core upon σ- and π-functionalisation are illustrated in Figs 24 and 25. It is clearly seen that the addition of any exopolyhedral fragment to a 6/6 bond results in its elongation and a specific redistribution of lengths of the neighbouring C–C bonds. The distortions of the

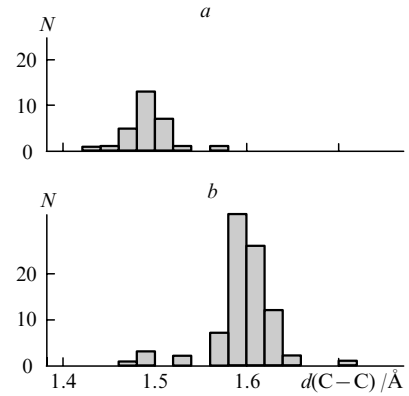


Figure 24. The distribution of lengths of the coordinated 6/6 C–C bonds in π- (*a*) and σ-derivatives of buckminsterfullerene (*b*).

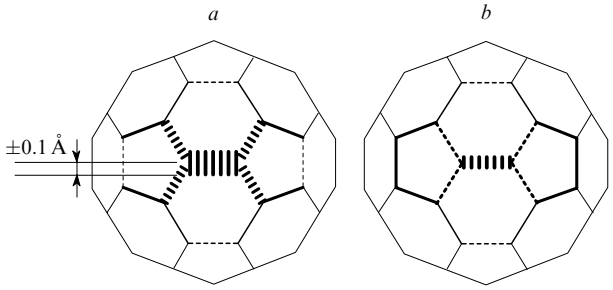


Figure 25. The elongation (dashed lines) and shortening (solid lines) of bonds in the fullerene molecule upon σ- (*a*) and π-addition (*b*). The magnitude of the bond length changes is proportional to the line width (the scale is shown).

C_{60} core due to coordination to a η^2-ML fragment (where M denotes a transition metal atom and L is its ligand shell) are substantially weaker as compared to those in σ-adducts, including $C_{60}CR_2$ derivatives. Note that the geometrical distortions of the cluster C_{60} are localised in the immediate proximity to the modified 6/6 bond both in σ- and π-derivatives, *i.e.*, the fullerene cage 'poorly transmits' the influence of attached fragments. As for chemically modified derivatives of C_{70}, structural data available for them are too sparse to derive reliable correlations.

A deeper chemical modification can result in opening and rearrangement of the carbon core. In particular, the molecule of a fullerene diketo derivative with an open 11-membered face admits penetration of small molecules, such as H_2, inside the fullerene core.[223] Another way to modify fullerene consists in 1,2-addition leading to the opening of the carbon cage and formation of a new fullerene with a four-membered carbocycle and two extra carbon atoms.[50] The cobalt complex σ,η^2,σ-$C_{64}H_4CoCp$, which contains an open fullerene core with a C_4H_4 fragment attached can be taken as an example.[224]

The crystal packings in chemically modified fullerenes obey the same regularities as molecular complexes. If a small externally attached fragment (*e.g.*, an oxygen atom) is present, a packing similar to the structure of pure C_{60} is formed. Covalently bound exopolyhedral fragments smaller than the van der Waals diameter of the fullerene sphere perform as 'diluents' in the standard structural motifs $(C_{60})_\infty$ (see Table 4). For instance, the crystal structure of the carbene monoadduct $C_{60}C(COOEt)_2 \cdot CHCl_3$ (ρ = 0.81)[225] may be classified as a three-dimensional framework with the MCN = 8 (here, the term MCN applies only to the fullerene subunit rather than to the whole molecule). At the same time, 3-benzyloxycarbonyl-(60)fullereno[1,2-*d*]isoxazole with the

bulkier five-membered isoxazole ring attached to the fullerene molecule, is composed of hexagonal layers of the C_{60} cores with the MCN = 6.[226] Bulkier exopolyhedral fragments together with solvate molecules result in looser packings down to motifs comprising isolated fullerene cores, such as the one encountered in the hexaadduct $C_{60}[C(COOEt)_2]_6$.[219] Note that fragments chemically attached to the fullerene core suppress rotational disorder, which typically leads to higher accuracy of the structure determination.

IX. π-Derivatives

The chemical properties of fullerenes as π-ligands are closer to polyalkenes rather than aromatic hydrocarbons. Chemically non-modified buckmisnterfullerene coordinates a few metal atoms by its 6/6 bonds acting exclusively as a η^2-ligand. As for σ-addition, η^2-coordination to one of the 6/6 bonds in buckminsterfullerene activates five analogous bonds forming together an octahedron over the fullerene cage (T_h symmetry, see Fig. 22 *f*). Upon π-coordination, the elongation of the affected 6/6 bond is not as significant as in the case of σ-addition (see Fig. 24). As a rule, the second group is π-coordinated at a *trans*-position with respect to the first one. The maximum number of metal-containing groups ML_n attached in this way is 6 (realised in the case of platinum), and the metal atoms are located in the vertices of an octahedron.[227]

Closely spaced double bonds enable fullerenes to act as polydentate η^2:η^2- and η^2:η^2:η^2-ligands in complexes with clusters of the platinum-group metals (Fig. 26). Such a coordination type is typical of arene ligands, *e.g.*, $C_6H_6Os_3(CO)_9$.[228] In a series of fullerene complexes with osmium and ruthenium, three metal atoms forming a triangular cluster are coordinated by three double bonds of one hexagonal face of the fullerene molecule.[229] A few complexes with buckminsterfullerene acting as a η^2-ligand for a triangular osmium carbonyl cluster have been reported.[230] In a series of closely related complexes described by Park *et al.*,[231] the osmium triangle coordinates fullerene as a η^2:η^2:η^2-, σ:η^2:σ- or η^2:η^2-ligand, depending on the non-fullerene ligand environment of the metal atoms.

In total, the CSD contains 30 entries, in which fullerene cages are π-coordinated to a single metal atom, 10 entries — to two metal atoms, 14 — to three, 2 — to four, 9 — to five and 6 — to six metal atoms. Furthermore, π-complexes containing two fullerene ligands coordinated to one cluster unit, such as Rh_6,[232] and even to one metal atom (Mo or W, see Fig. 26 *e*) [233] are known. For the π-complex $(\eta^2\text{-}C_{60})Ir(o\text{-}C_2B_{10}H_{10}CH_2PPh_2)(Bu^tNC)_2$, which contains the carborane and fullerene moieties coordinated to one iridium atom, insertion of an O_2 molecule at the metal–carbon bond upon oxidation in air has been confirmed by single-crystal X-ray diffraction. The resultant five-membered peroxide metallacycle has an Ir–C σ-bond with a length of 2.24 Å (Fig. 27).[52]

A η^2-coordination of an ML fragment to the fullerene core results in a redistribution of the C–C bond lengths, which is similar to that observed upon σ,σ-addition, but is less pronounced. Upon π-coordination, the 6/6 bond involved is elongated, on the average, to 1.48 Å (as compared to 1.60 Å in $C_{60}X_2$). The adjacent 5/6 bonds are elongated to 1.49 Å and a redistribution of the lengths of the adjacent bonds takes place (see Fig. 25). As in the case of σ-derivatives, the influence of the η^2-coordination on neighbouring bonds quickly attenuates with increasing distance from the coordinated bond and the 'rear' hemisphere of the fullerene core remains virtually unaffected.

In a series of structurally similar mononuclear fullerene complexes with iridium (fullerene)·$[Ir(CO)Cl(PPh_3)_2]_n$, n = 1, 2 (fullerene = C_{60}, $C_{60}O$, C_{70}, $C_{70}O$, C_{84}), the iridium atoms have approximately trigonal bipyramidal coordination environment. Essential geometrical parameters of these complexes are given in Table 6. Note that the volume occupied by the fullerene ligand in the coordination environment of iridium is larger than that of the triphenylphosphine ligand (the P–Ir–P bond angle is less than 120°, see Table 6).

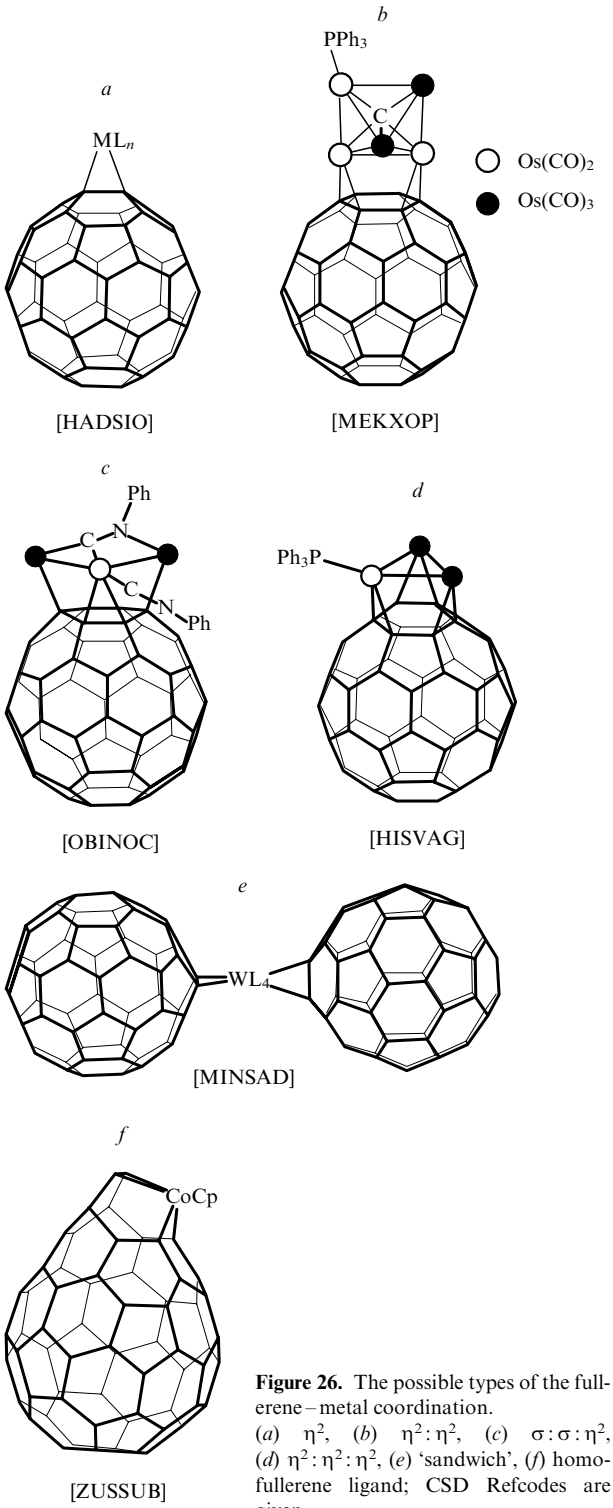


Figure 26. The possible types of the fullerene–metal coordination.
(*a*) η^2, (*b*) η^2:η^2, (*c*) σ:σ:η^2, (*d*) η^2:η^2:η^2, (*e*) 'sandwich', (*f*) homofullerene ligand; CSD Refcodes are given.

Penta-functionalised fullerene derivatives $C_{60}R_5$, in which the attached groups are located around a five-membered ring, are similar in terms of their electronic structure to pentasubstituted cyclopentadiene and thus can be involved into the η^5-coordination. In the structurally chracterised thallium salt $C_{60}Ph_5^-$,[238] which is analogous to cyclopentadienyl complexes of alkali metals with the essentially ionic metal–ligand bonding of the η^5-type, the

Table 6. The geometrical parameters of the coordination environment of iridium atoms in the (η^2-fullerene)·Ir(CO)Cl(PPh_3)$_2$ π-complexes.

Fullerene	Ir–C /Å	Ir–CO /Å	Ir–Cl /Å	Ir–P /Å	P–Ir–P /deg	Cl–Ir–CO /deg	Ref.
C_{60}	2.190	1.923	2.401	2.384	113.4	179.7	234
C_{60}/2	2.171	1.852	2.410	2.330	109.8	175.8	235
$C_{60}O$	2.172	1.840	2.396	2.386	113.5	179.0	176
C_{70}	2.182	1.834	2.362	2.384	114.9	178.8	236
C_{70}/2	2.176	1.838	2.366	2.356	104.2	176.1	237
$C_{70}O$	2.234	1.845	2.355	2.364	114.5	178.7	178
C_{84}	2.197	1.824	2.418	2.376	114.7	178.4	33

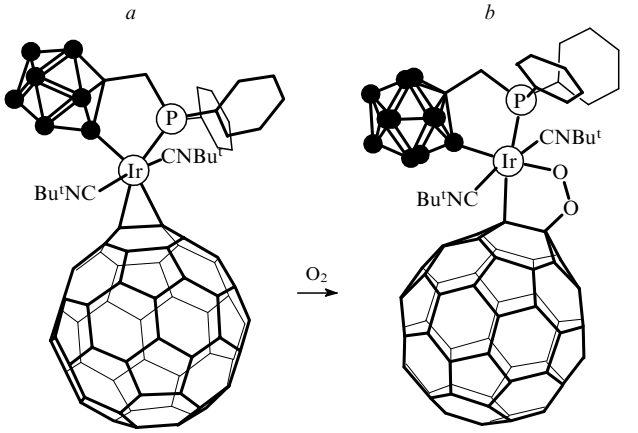


Figure 27. The molecular structures of the carborane–fullerene π-complex of iridium η^2-C_{60}Ir(*o*-$C_2B_{10}H_{10}CH_2PPh_2$)(Bu^{t}NC)$_2$·4 PhMe (*a*) and the product of its air oxidation (*b*) (single-crystal X-ray diffraction data).[52]

Tl–C lengths lie in the range 2.83–2.89 Å. The thallium atom is additionally coordinated to an oxygen atom of the THF solvate molecule at a distance of 3.16 Å. In another rhodium-based complex $C_{60}Me_5Rh(CO)_2$, the $C_{60}Me_5$ core acts as a real η^5-ligand coordinated to a metal atom[239] with the bonding Rh–C distances in the range of 2.12–2.27 Å.

As in the case of σ-addition, the fullerene C_{70} π-coordinates external metal atoms most typically by the *b* type bonds or, in complexes with metal clusters or several independent metal atoms, by *b* and *d* type bonds (see Fig. 1 *b*). In the thallim derivative $C_{70}(C_6H_4CF_3)_3Tl\cdot o$-$C_6H_4Cl_2$, the $C_{70}(C_6H_4CF_3)_3$ fragment acts as a cyclopentadienyl-like anion.[240] The molecular structures of the η^5-coordinated derivatives of C_{60} and C_{70} are depicted schematically in Fig. 28.

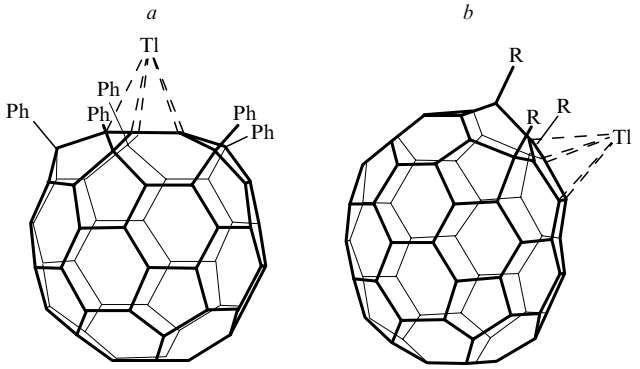


Figure 28. Examples of the η^5-coordination fullerene–metal. (*a*) $C_{60}Ph_5Tl\cdot 2.5\,THF$, Tl–C = 2.83–2.89 Å (see Ref. 238), (*b*) $C_{70}(C_6H_4CF_3)_3$ $Tl\cdot C_6H_4Cl_2$, Tl–C = 2.84–3.08 Å (R = *p*-$C_6H_4CF_3$).[240]

The D_{2d} isomer of C_{84} in the structurally investigated complex $C_{84}\cdot Ir(CO)Cl(PPh_3)_2$ is coordinated to iridium through the 6/6 bond located at the intersection of two symmetry planes. The coordinated bond is elongated to 1.45 Å, and the spherical excesses of its carbon atoms are increased to 21° and 18°.[33]

Of particular interest are the structures and chemical properties of fullerene metallocomplexes containing metal atoms bound to strongly modified 'open' carbon cages and involving attached exopolyhedral functional groups. For instance, the cobalt atom in the crystal structure of $C_{60}C_4H_4CoCp\cdot C_7H_8$ is coordinated to bishomofullerene acting as a (η^2,σ,σ)-ligand (see Fig. 26 *f*).[82] In this compound, the fullerene cage is open due to the formation of an 11-membered ring.

Bulky and sterically flexible molecules of fullerene π-complexes often form several different solvates with the same solvent. A typical example is two benzene solvates of the complex $C_{60}[Ir(CO)Cl(PPhMe_2)_2]_2$ (Fig. 29).[235] In one of the solvates with the composition $C_{60}[Ir(CO)Cl(PPhMe_2)_2]\cdot C_6H_6$ (ρ = 2.21), the fullerene cores are isolated from each other while in the second complex, which is characterised by the stoichiometry $C_{60}[Ir(CO)Cl(PPhMe_2)_2]\cdot 2\,C_6H_6$ (ρ = 2.45), the packing of fullerene fragments may be described as separated columns.

It is convenient to describe the crystal packings encountered in fullerene π-complexes (as well as in other derivatives) in terms of motifs formed by fullerene spheres. A distinctive feature of the π-complexes is an appreciable volume of the non-fullerene part. This often gives rise to loose and isolated motifs. Fullerene π-complexes with palladium and platinum having the composition $C_{60}M_n$ (attributed in the present review to fullerides) represent an exception from this tendency.

X. Endohedral fullerenes

Endohedral fullerenes, *i.e.*, compounds containing different 'guests', such as metal or nonmetal atoms (including atoms of inert gases) or small cllusters, inside the carbon cage, take a special place among diverse fullerene derivatives. The regularities of the formation of these compounds have been reviewed by Shinohara[241]. Endohedral metallofullerenes (EMFs) have been detected by mass spectrometry for the first time simultaneously with the 'empty' fullerenes,[242] and later were isolated in microgram quantities.[243] However, structural studies of these species are impeded to a great extent by their high reactivity and the multitude of isomers (see below).

A heating of 'empty' fullerenes C_n in the atmosphere of an inert gas A under pressure allows preparation of endohedral§ derivatives A@C_n in trace amounts.[244] In particular, endohedral compounds of C_{60} with ^{3}He (see Ref. 245) and ^{129}Xe (see Ref. 246) were prepared and studied by NMR. In the case of C_{70}, endohedral derivatives $A_2@C_{70}$ [A = He (see Ref. 247) and Ne (see Ref. 248)] with two inert gas atoms inside the fullerene cage were produced using this route. The ratio between the products A@C_{70} and $A_2@C_{70}$ suggests the 'classical' mechanism of the synthesis involving cleavage of a C–C bond with subsequent closure of the

§ In chemical formulas, the endohedral component is denoted with the sign @.

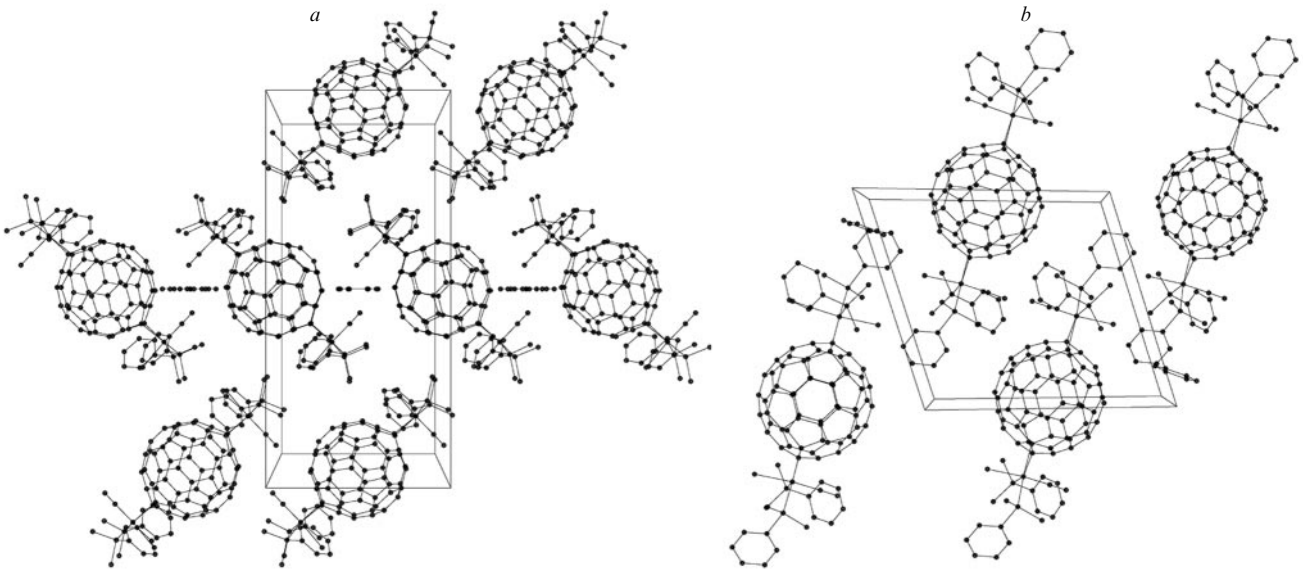


Figure 29. The molecular packings in the crystal structures of $C_{60}\cdot[Ir(CO)Cl(PPhMe_2)_2]\cdot C_6H_6$ (*a*) and $C_{60}\cdot[Ir(CO)Cl(PPhMe_2)_2]\cdot 2\,C_6H_6$ (*b*).[235]

cage. The single-crystal X-ray diffraction study of a solid solution of $Kr@C_{60}$ in crystalline $C_{60}\cdot NiOEP\cdot 2\,C_6H_6$ has shown that the krypton atom is located in the centre of the fullerene cage at distances of 3.54 Å from carbon atoms (which is 0.2 Å shorter than the sum of their van der Waals radii). The fraction of $Kr@C_{60}$ in the single crystal was estimated to be 9% based on the refinement of the Kr position occupancy.[249] A series of endohedral derivatives $X@C_{60}$ [where X = Li (see Ref. 250), N (see Ref. 251) and P (see Ref 252)] have been synthesised using an ion bombardment of C_{60} films *in vacuo* and studied with ESR. For the two latter cases, it was shown that the atoms of the fifth-group elements do not bind to the walls of the carbon cage and thus are in the quadruplet state, *i.e.*, have three unpaired electrons.

The standard method of the synthesis of endohedral metallofullerenes consists of a plasma-induced sublimation of graphite impregnated with the corresponding metal oxide (1 at.% – 2 at.%) in a helium atmosphere (10 – 100 Torr). Mass spectra of the products synthesised, in addition to C_{60}^+ and C_{70}^+, reveal peaks attributable to MC_n^+ ions ($n = 60-100$) with the predominance of MC_{60}^+ and MC_{82}^+.[241] Using extraction with polar organic solvents or CS_2 followed by chromatographic separation, the endohedral derivatives $M@C_{82}$, $M@C_{84}$ and $M_2@C_{80}$ moderately stable in air can be isolated while pure $M@C_{60}$ is very difficult to isolate due to its high reactivity. Individual EMFs of more than 20 metals (predominantly, lanthanides) have been synthesised to date in milligram quantities.[253 – 256]

One of the factors hampering the structural studies of EMFs (as well as of 'empty' higher fullerenes) is the isomerism of their carbon cores.[253] Quantum chemistry calculations on EMFs revealed a substantial charge transfer from the metal atoms to the carbon cage, which stabilises higher-symmetry isomers and can even result in a violation of the isolated pentagon rule.[257] Quantum chemistry optimisation of the geometry of mononuclear endohedral metallofullerenes $M@C_n$ predicts a shift of the metal atom from the centre of the cavity towards the walls giving rise to the bonding intrapolyhedral M···C contacts with lengths ~ 2.5 Å and a large molecular dipole moment (4 – 5 D). Furthermore, quantum chemistry calculations and spectroscopic data show the easiness of the metal atom migration inside the carbon cage, which poses additional difficulties for the structural studies.[19, 253, 257, 258]

The most studied mononuclear lanthane derivative $Ln@C_{82}$ represents, according to the spectral data,[256] a mixture of isomers with the C_{2v} (isomer I, content 70% – 80%) and C_{3v} symmetry (isomer II, content 20% – 30%) (Fig. 30). For derivatives of some other metals, the isomers III (Er, Dy, Tm, Ca) and IV (Ca) were

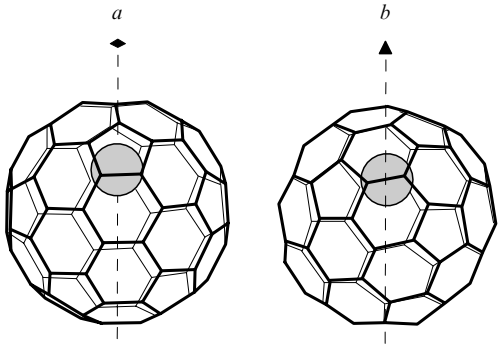


Figure 30. The molecular structures of endohedral metallofullerenes having the isomeric C_{82} cores with the C_{2v} symmetry (*a*) and the C_{3v} symmetry (*b*) (quantum-chemistry calculations).[253]

additionally found.[256, 259] Therefore, in order to avoid a thorough statistical disorder in single crystals, preparation of endohedral metallofullerenes for structural studies should always involve a time-consuming stage of the chromatographic separation of isomer mixtures.

For the majority of endohedral fullerenes, experimental data on their structures have been obtained by means of XAFS spectroscopy [260 – 264] and powder X-ray diffraction utilising synchrotron radiation. The position and overall shape of the X-ray Absorption Near-Edge Structure (XANES) spectra confirm the intramolecular charge transfer from the 'guest' metal atoms to the carbon cage. A shift of the metal atom from the centre of the fullerene cage and its coordination to carbon atoms have been established experimentally for the first time in the EXAFS studies of $Y@C_{82}$ (see Ref. 261) and $La@C_{82}$ (see Ref. 262). In mononuclear actinide-based (Th, U and so forth) endohedral derivatives of fullerenes $C_{82}-C_{84}$, the charge of the metal ions was estimated as 3+ according to the results of XANES.[265]

The most essential details of the molecular and crystalline structures for a series of polycrystalline EMFs were determined in an extended series of diffraction studies [85, 264 – 270] based on the maximum entropy method (MEM). For all the studied phases, the insertion of metal atoms into carbon cages was objectively revealed. Preparation of the binuclear derivative $Sc_2@C_{66}$ has been reported, in which the geometry of the carbon cage does not obey the IPR, in agreement with the quantum chemistry calcu-

lations.[15] In the strongly disordered crystal structure of $Sc_2C_2@C_{84}$ (see Ref. 271), a carbide cluster with two carbon atoms at a distance of 1.42(6) Å has been revealed inside the fullerene cage. The metal–metal distances in binuclear $La_2@C_{80}$ (3.90–3.94 Å)[271] and $Sc_2@C_{84}$ (3.91 Å)[268] derivatives imply that there is no direct metal–metal bonding. On the other hand, the Sc–Sc bonds with a length of 2.89 Å are revealed in $Sc_2@C_{66}$, which has a smaller carbon cage.[15] Furthermore, abnormally short Sc–Sc bonds with the length of 2.3(3) Å (see Ref. 270) (as compared to 3.20–3.30 Å in bulk scandium[272]) were found in the (1 : 1) toluene solvate of the three-nuclear derivative $Sc_3@C_{82}$. This result contradicts to the quantum chemistry calculations[257] and is probably caused by a rotational disorder of the EMF molecule. Estimates of charges of the endohedral fragments obtained by integrating the electron density distribution reconstructed from the powder X-ray diffraction data[15,85,270,272] are doubtful since they lie far beyond the standard accuracy of the technique. Notwithstanding, these studies report very important structural information concerning EMFs at a semiquantitative level.

A series of endohedral fullerenes, $M_3N@C_n$ (M = Sc, Er; n = 78, 80, 68), which have been synthesised and characterised by single-crystal X-ray diffraction,[16,273–275] contain triangular nitridometal clusters inside the respective carbon cages. They were produced through the plasma evaporation route in a dynamical N_2-containing atmosphere and crystallised as (1 : 1) molecular complexes with cobalt octaethylporphyrinate CoOEP also contaning solvent molecules. Despite the presence of short intermolecular Co···C (fullerene) contacts in the range of 2.71–2.78 Å, fullerene moieties and endohedral M_3N 'guest' fragments are strongly rotationally disordered. The molecular structures of two high-symmetry isomers of C_{78} (D_{3h}) and C_{80} (I_h) stabilised by a charge transfer from the metal atoms were established. The geomertry of the endohedral M_3N fragment (Fig. 31) was determined and a lability of the M···C (fullerene) bonding was pointed out. The same group of authors reported the preparation and crystal structure study of the dimethoxyxylylene derivative $Sc_3N@C_{80}$Dmxy.[276] In this structure, the fullerene cage is chemically modified from the outer side through a [4 + 2] cycloaddition to a 5/6 bond, which results in its elongation to 1.63 Å, but the endohedral group is nevertheless disordered. As has been determined, in the case of the C_{78} core, endohedral metal atoms are located above the 6/6 bonds of the pyracylene fragment, in agreement with the quantum-chemical predictions.[277] Meanwhile, in the case of the C_{80} core, which has no pyracylene fragments, the endohedral M_3N group is chracterised by a stronger rotational disorder. A smaller endohedral fullerene isolated and studied by single-crystal X-ray diffraction as a complex with the analogous composition, likely contains the C_{68} core that violates the isolated pentagon rule.[16] Both the fullerene cage and the endohedral fragment in this substance are strongly disordered, its stoichiometry was confirmed by mass spectrometry.[16]

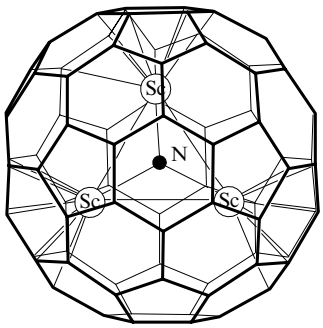


Figure 31. The molecular structure of $Sc_3N@C_{80}$ (single-crystal X-ray diffraction data).[273]
Interatomic distances: Sc–N 2.00–2.01 Å, Sc–C 2.15–2.73 Å, Sc–Sc 3.48 Å.

A single-crystal X-ray diffraction study of another endohedral metallofullerene molecular complex $Er_2@C_{82}\cdot CoOEP\cdot(C_6H_6)_{2-x}\cdot(CHCl_3)_x$ revealed[278] a carbon cage of the C_s symmetry and a strong disorder of the erbium atoms over numerous positions. The second isomer of this substance with the C_{3v} symmetry of the carbon core and the disordered endohedral fragment was also prepared and characterised.[279]

Solvent-free EMFs at room temperature are characterised by an fcc lattice[280] isomorphous to that of high-temperature modifications of C_{60} and C_{70}. Upon slow cooling, $La@C_{82}$ single crystal undergoes two phase transitions due to orientational ordering of the ellipsoid EMF molecules giving rise to the rhombohedral (180–150 K) and metastable triclinic (150–20 K) modifications. Rapid cooling of the rhombohedral polymorph yields a disordered simple cubic phase, which is stable below 132 K.[280] In strongly disordered EMF solvates $M@C_{82}\cdot 1.5\,CS_2$, the carbon disulfide molecules occupy cavities within a bcc lattice. This phase undergoes a magnetic phase transition at 150 K, which was suggestively attributed to the ordering of the metal-containing fullerene cores.[281] Endohedral fullerene derivatives, like pure fullerenes, are able to polymerise at elevated pressures.[282]

According to the powder X-ray diffraction data, monoclinic toluene solvates $M@C_{82}\cdot PhMe$ are isomorphous to the respective solvates of 'empty' higher fullerenes $C_{82}\cdot PhMe$ and $C_{76}\cdot x\,PhMe$.[31] The molecular packing motif in these structures conforms to that found earlier in the (1 : 1) solvates of buckminsterfullerene with n-pentane, dichloroethane and other solvents[84] (see Fig. 6) but the intermolecular electrostatic interactions favour the 'head-to-tail' arrangement of neighbouring molecules in the case of the endohedral derivatives.[267] The crystal structures of the $M_3N@C_{80}\cdot CoOEP\cdot Solv$ complexes discussed above contain zigzag chains of fullerene cages similar to those in molecular complexes of C_{60} and C_{70} with metalloporphyrins (see Fig. 8). The shortest distance between the centres of fullerene cores in the EMFs with known crystal structures lie in the range of 11.00–11.22 Å.

XI. Conclusion

The distinctive features of crystal chemistry of fullerenes summarised above are defined primarily by the involvement of bulky spherical-like carbon clusters and the predominance of non-bonding intermolecular interactions. The results of structural investigations into various derivatives of fullerenes including chemically modified and endohedral ones demonstrate the typical rotational disorder of carbon cores (which can be attenuated down to a complete ordering at low temperatures), high affinity of fullerenes towards formation of molecular complexes and diversity of their crystalline phases. Patterns of the rotational disorder typical of C_n molecules in crystals can be conveniently described within the model of the 'rubber cavity', which postulates occurrence of specific orientations corresponding to local minima of the shallow interaction potential. In all the considered classes of compounds, similar motifs of arangement of fullerene cores are observed, which are defined by the volume fraction occupied by the fullerene component in the total unit cell volume. Non-fullerene molecules and exopolyhedral fragments fill cavities of these motifs thus acting as a flexible van der Waals matrix.

Coulomb attraction (in ionic fullerides) and specific intermolecular interactions stabilise the crystal packing and increase the degree of ordering, which enables collection of more accurate crystallographic data for the corresponding substances. Some authors suggest weak Jahn–Teller distortions in mono- and dianions of buckminsterfullerene and proneness of anionic fullerenes to polymerisation. Chemical bonding between two or more fullerene molecules gives rise to dimers and trimers as well as to infinite motifs composed of chain, layer and framework polymeric structures.

The presence of 'guest' atoms inside the fullerene cages in the case of endohedral derivatives can, on the one hand, stabilise the crystal packing due to the polarisation of the carbon clusters and, on the other hand, increase structural disorder due to multiple positions of the endohedral atoms and/or dynamical transitions inside the carbon cage. According to the quantum chemistry calculations and experimental spectral data, endohedral metallofullerenes are characterised by a metal → carbon cage charge transfer stabilising the higher-symmetry isomers. Additional degrees of freedom in endohedral metallofullerenes, such as molecular dipole moment or magnetic moment of the 'guest' atoms, increase the number of possible ordering types and respective phase transitions.

The most typical way of a chemical modification of fullerenes (to form either σ- or π-derivatives) consists of an addition to one of the 6/6 bonds, which is accompanied by its elongation and a specific distortion of the carbon cage localised in the proximity to the exopolyhedral coordinated atoms. In the case of C_{70}, a functionalisation preferably occurs at the stereochemically strained and the most 'pyramidised' *b* type 6/6 bond. For several C_{60} and C_{70} derivatives, the addition occurs at a 5/6 bond and results in its cleavage and formation of 'open' homofullerene cages. As compared to crystals of non-modified fullerenes, functionalised derivatives are typically better ordered owing to the nonsphericity of their molecular shapes.

The multiple σ,σ- or η^2-addition of exopolyhedral fragments not interacting with each other proceeds at the most distant 6/6 bonds ultimately yielding (in the case of C_{60}) hexadducts with six exopolyhedral fragments octahedrally surrounding the fullerene core. If a metal cluster is taken as the exopolyhedral fragment, the fullerene molecule can act as a polydentate π-ligand coordinating the cluster through one of its hexagonal faces. In the case of σ-modified fullerenes, the η^5-coordination to single metal atoms is possible and even η^6-bonding can be realised in the future. Multiple σ-addition of small exopolyhedral fragment X leads to 'binary' fullerene derivatives C_nX_m (n = 60, 70; X = H, O, F, Cl, Br, Me, CF_3). When the number of attached fragments m is small (up to 5–6), they are typically localised in the same specific part of the carbon cage. Meanwhile, a more profound modification is accompanied by spreading of the attached groups X over the fullerene hemisphere (*e.g.*, in $C_{60}F_{18}$ and its analogues) or the entire sphere (*e.g.*, in $C_{60}Br_{24}$, $C_{60}F_{36}$ and $C_{60}F_{48}$). A deep chemical modification induces substantial distortions of the fullerene polyhedral cage and can even result in its opening.

The present structural data survey is in part a result of our own research activities, which have been conducted starting from the second half of the 1990s. We are grateful to all our colleagues who provided us with single crystals of new substances synthesised in their laboratories and shared with us the most recent structural results of their own (sometimes even prior to publication). We thank Corresponding Member of RAS M Yu Antipin (INEOS RAS, Moscow), Profs. G Saito (University of Kyoto, Japan), O Kashino and I Kubozono (Okayama University, Japan), R N Lyubovskaya (IPPC RAS, Chernogolovka), M V Korobov and O V Boltalina (Department of Chemistry, MSU, Moscow), J Howard (University of Durham, UK), R Taylor (University of Sussex, UK) and Dr. D V Konarev (IPCP RAS, Chernogolovka). Very interesting and useful information was collected owing to our participation in the series of the biannual international conferences IWFAC (International Workshop 'Fullerenes and Atomic Clusters') held in St Petersburg.

This review has been prepared and written with financial support of the Russian programme 'Fullerenes and Atomic Clusters' and the Russian Foundation for Basic Research (Project No. 02-03-33225).

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