Russian Chemical Reviews **68** (1) 19 – 38 (1999) © 1999 Russian Academy of Sciences and Turpion Ltd

UDC 593.194 + 547.435

Donor – acceptor complexes and radical ionic salts based on fullerenes

D V Konarev, R N Lyubovskaya

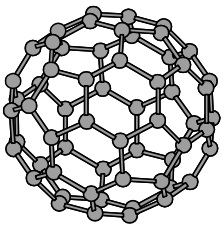
Contents

I.	Introduction	19
II.	Fullerenes	20
III.	Donor – acceptor complexes and radical ionic salts of fullerenes	21
IV.	Structure and spectral characteristics of complexes and radical ionic salts of fullerenes	30
V.	Conclusion	35

Abstract. The review generalises for the first time the published data on the synthesis and properties of donor-acceptor type of compounds based on fullerenes, various solvates and clathrates, inclusion compounds, molecular complexes and charge-transfer complexes both with inorganic donors and with organoelement donors of the tetrathiafulvalene, amine, metallocene and metalloporphyrin series. Radical ionic salts of fullerenes with bulky cations and alkali metals obtained by intercalation or by direct synthesis in solution are discussed. Results of studies of fullerene compounds by IR, optical, ESR, X-ray photoelectron and ^{13}C NMR spectroscopy, as well as their conducting (including superconducting), magnetic and optical properties are discussed. The bibliography includes 208 references.

I. Introduction

The discovery of fullerenes, a new allotropic modification of carbon, in the mid-80's [1] confirmed the prediction of theorists [2, 3] on the possible existence of polyhedral carbon molecules with icosahedral symmetry.

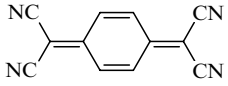


In the early 90's, a simple method to obtain fullerene C_{60} in gram amounts was found; this gave an impetus to more detailed studies of physical and chemical properties of the C_{60} clusters and compounds based on them.[4] The number of works in this area grows steadily, and they cover an ever wider range of fundamental and applied branches of science and technology. In 1996, Kroto, Smalley and Curl were awarded the Nobel Prize in chemistry for the discovery of fullerene and for their great contribution to the development of this area.

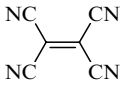
D V Konarev, R N Lyubovskaya Institute for Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax (7-096) 515 35 88. Tel. (7-096) 517 18 52. E-mail: konarev@icp.ac.ru (D V Konarev), lyurn@icp.ac.ru (R N Lyubovskaya)

Received 26 May 1998
Uspekhi Khimii **68** (1) 23 – 44 (1999); translated by S S Veselyi

Generally, fullerenes display acceptor properties[5 – 7] and can be regarded as π-acceptors. They can form various donor – acceptor (D – A) non-covalent compounds, similar to the well-known planar π-acceptors, *e.g.*, tetracyanoquinodimethane **1** (TCNQ), tetracyanoethylene **2** (TCNE), *p*-quinone, *etc.*[5, 8]



1



2

These D – A compounds are formed due to rather weak (in comparison with the standard covalent chemical bonds) van der Waals interactions and due to charge transfer from the donor to the acceptor.[9] Charge transfer plays a very important role and results in qualitatively new physicochemical properties of these compounds. D – A compounds can be divided into several groups according to the degree of charge transfer (δ), although there is no distinct boundary between these groups. The compounds with δ close to zero can be attributed to molecular complexes. In the case of partial charge transfer from the donor to the acceptor ($0 < \delta < 1$), charge-transfer complexes (CTC) $D^{\delta+}A^{\delta-}$ are formed. For example, in the TTF – TCNQ complex, where TTF is tetrathiafulvalene, different estimates give $\delta = 0.48 - 0.67$.[8] A characteristic feature of CTC is the appearance of a new band in the absorption spectrum of the complex in the visible and near IR regions due to the transfer of an electron from the donor to the acceptor when absorption of a light quantum occurs.[9] In the extreme case, *i.e.*, in the complete charge transfer from the donor to the acceptor or in the formation of a compound from oppositely charged ions, radical ionic salts $D^{n+}A^{n-}$ are formed (in the case of radical ionic salts of fullerenes, n is an integer).

The charge-transfer complexes and radical ionic salts based on planar polyconjugated heterocyclic π-donors and acceptors are being intensely studied lately. Many of them, the so-called organic metals, have unique conduction and magnetic properties.[10, 11]

Radical cationic salts of tetrathiafulvalene derivatives draw special attention. The majority of organic metals and superconductors obtained to date correspond to this class of compounds.[10, 11]

The discovery of fullerene has given the researchers a new π-acceptor with a number of essential features that distinguish it from other acceptor molecules: larger size, spherical shape, unique electronic structure, high symmetry and polarisability. The resulting specific features of donor-acceptor interactions in compounds of the C_{60} fullerene enabled the design of materials with

unusual physical properties. For example, it was found that intercalation of C_{60} by alkali metals results in superconductors with composition M_3C_{60} (M = K, Rb, Cs) with rather high superconductivity transition temperatures (T_c) ($18 \leqslant T_c \leqslant 40$ K).[12–14] The salt of C_{60} with an organic donor, tetrakis(dimethylamino)ethylene (TDAE), is a ferromagnetic with $T_c = 16.1$ K,[15] and apparently has superconducting properties.[16] Combination of conducting polymers with fullerene enables efficient phototransfer and separation of charges with long lifetime, which increases considerably the photoconductivity of polymers and can be utilised in xerography and energy phototransducers.[17]

By now, a considerable number of various D–A compounds of fullerenes have been obtained, including molecular complexes, CTC and radical ionic salts with different states of oxidation or reduction. The C_{60} fullerene molecule can accept up to 12 electrons[13, 14, 18] and release one electron,[7] *i.e.*, the charge of the C_{60} molecule can vary from +1 to −12. As a result, C_{60} compounds manifest a broad spectrum of properties.

The considerable interest of experts from different areas in fullerenes and compounds based on them is reflected in a number of books and reviews.[19–28] In particular, the reviews are devoted to chemistry,[21] spectroscopy[22–26] and magnetic properties[27] of fullerenes and compounds based on them, as well as to intercalation of fullerenes with alkali and alkaline-earth metals.[13, 14, 28]

The present review generalises for the first time the published data on the synthesis of D–A compounds based on fullerenes that are formed both through van der Waals interaction and charge transfer. These include solvate and clathrate compounds, inclusion compounds, molecular complexes, CTC and radical ionic salts of fullerenes with organic and organometallic donors and various metals. Data on IR, electronic, ESR, X-ray, photoelectron and ^{13}C NMR spectroscopy are considered. The features of D–A complexes and radical ionic salts of fullerenes, including superconducting, magnetic and optical properties, are discussed.

II. Fullerenes

1. Features of fullerene structure

It is known that the molecule of the C_{60} fullerene has icosahedral symmetry (group I_h), and its surface consists of 20 six- and 12 five-membered rings.[1]

The molecule of the C_{70} fullerene consists of 25 six-membered and 12 five-membered rings. It has an elongated shape and lower symmetry (D_{5h}). Higher fullerenes also represent polyhedral molecules and contain a larger number of hexagonal facets.[25]

All 60 carbon atoms in the C_{60} molecule are equivalent, which is confirmed by the presence of a single signal in the ^{13}C NMR spectrum.[29] The mean C–C distance in C_{60} (1.44 Å) is close to the C–C distance in graphite (1.42 Å). Each carbon atom in the C_{60} molecule is linked to three other carbon atoms by two longer 6–5 bonds in five-membered rings and by one shortened 6–6 bond, which is common to two fused six-membered rings. Thus, the carbon atoms in C_{60} have a near-sp^2 hybridisation.[25, 30]

Usually, the symmetry axis of the π-orbital is orthogonal ($\Theta_{\sigma\pi} = 90°$) to the plane of the three σ-bonds in the sp^2 hybridisation. Because of the spherical shape of the C_{60} fullerene molecule, the four mutually linked carbon atoms do not lie in the same plane and the angle $\Theta_{\sigma\pi}$ is 101.64° rather than 90°.[30] Thus, pyramidalisation of carbon atoms occurs in fullerenes, which results in significant strain in the fullerene molecule and changes the character of the π-orbitals; thus, there is certain contribution by a σ-orbital to the π-orbitals of all fullerenes. Pyramidalisation affects strongly the electronic properties of fullerenes and predetermines their high electron affinity, as the strain in the molecule is partially eliminated upon reduction of fullerenes.[30]

2. Donor–acceptor properties and polarisability of fullerenes

The ionisation potentials (IP),[25] electron affinities (EA)[6] and the corresponding redox potentials (E_{Ox}, E_{Red})[31] of the C_{60}, C_{70} and C_{76} fullerenes are listed in Table 1.

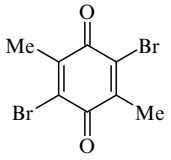
Table 1. Vertical electron affinity (EA),[6] first and second reduction potentials of fullerenes (E^1_{Red} and E^2_{Red}),[31] ionisation potentials (IP)[25] and oxidation potentials of fullerenes (E^1_{Ox}).[7]

Fullerene	EA/eV	E^1_{Red} /V [a]	E^2_{Red} /V [a]	IP /eV	E^1_{Ox} /V [b]
C_{60}	2.67	−0.44	−0.82	7.58	+1.26
C_{70}	2.68	−0.41	−0.80		+1.20
C_{76}	2.86	–			+0.81

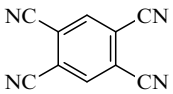
[a] CH_2Cl_2, SCE, 0.05 M $Bu^n_4NBF_4$; [b] relative to Fc/Fc^+ (Fc is ferrocene).

The first redox potentials of the C_{60} and C_{70} fullerenes in the polar solvents are close to each other. The redox potential of the $C_{60}/C_{60}^{-\bullet}$ pair is −0.44 V in dichloromethane and acetonitrile[5, 31] and −0.33 V in tetrahydrofuran[32] relative to the saturated calomel electrode (SCE). These values are 0.6–0.7 V smaller than the corresponding redox potentials of TCNQ (+0.22 V) and TCNE (+0.28 V).[5] Changing the polarity of the solvent shifts the redox potential of C_{60} insignificantly. For example, the redox potential in nonpolar benzene is −0.36 V relative to SCE.[32]

The C_{60} fullerene is rather a weak acceptor. The EA of C_{60} in the gas phase is 2.67 eV.[6] The adiabatic EA of C_{60} in solution (estimated from the energy of charge transfer and redox potentials) is much lower and equals 2.10–2.20 eV.[5] These values are comparable with the EA of such weak acceptors as 3,6-dibromo-2,5-dimethylquinone (**3**) or 1,2,4,5-tetracyanobenzene (**4**) (2.1 eV) but are much lower than those of TCNQ (2.82 eV) and TCNE (2.90 eV).[5]



3



4

One possible way to increase the EA is the introduction of strong acceptor substituents in fullerenes. It has been shown[33, 34] that halogenated fullerenes have stronger acceptor properties than C_{60}. For example, the theoretically calculated EA for $C_{60}Br_8$ is ~4.0 eV.[33] Fluorinated fullerenes, *viz.*, $C_{60}F_{36}$, $C_{60}F_{48}$ and $C_{70}F_{54}$, have considerably more positive first redox potentials than the corresponding fullerenes (−0.05, +0.51 and +0.76 V, respectively, relative to an Ag/Ag^+ reference electrode in dichloromethane).[34] The electron affinities of $C_{60}F_{36}$ and $C_{60}F_{48}$ are also higher than that of C_{60} (3.48 and 4.06 eV, respectively).[34] Functionalisation results in significant changes in the symmetry and electron structure of the C_{60} fullerene.[33]

Fullerenes, especially C_{60}, have high oxidation potentials. The ESR method detected the formation of the C_{60} radical cation in solutions containing strong oxidants,[35] but individual compounds in which C_{60} is charged positively have not been isolated yet.

Higher fullerenes possess higher electron affinities, and thus they are stronger acceptors. The C_{76} fullerene and other higher fullerenes undergo oxidation a little more readily than C_{60}.[7] For example, C_{76} is oxidised with hexabromocarboranyltris(2,4-dibromophenyl)ammonium (E_{Red} = +1.16 V) to give a radical cationic salt with positive charge on the fullerene.[7]

The polarisability of the C_{60} fullerene molecule is high ($\alpha \sim 85$ Å)[36] and is several times higher than that of other π-acceptors. Therefore, polarisation van der Waals forces are essential in the formation of D–A complexes and radical ionic salts of fullerenes.

3. Features of the crystal structure of C_{60} fullerene

At room temperature, C_{60} has a face-centred cubic (FCC) lattice.[37] The shortest distance between the centres of the C_{60} molecules in a crystal is 10.02 Å, which is smaller than the van der Waals diameter of the C_{60} molecule, considering the size of its π-electron cloud (10.18 Å, Ref. 25), hence the π-orbitals of the C_{60} molecules in a crystal overlap little. The weakness of interactions between the fullerene molecules in the solid state is the reason for the fast isotropic rotation of the C_{60} molecules in the crystal. Below 255 K, C_{60} crystals undergo a phase transition from the face-centred cubic lattice to a simple cubic lattice.[37] The rotation of the fullerene molecules in these crystals becomes anisotropic, it slows down, gets synchronised and occurs ratchet. In the case of such rotation, adjacent C_{60} molecules can be present in two different orientations relative to each other, which have different energies. In the first orientation, the shortened 'double' bond of one C_{60} molecule is located above the electron-deficient pentagonal facet, whereas in the second orientation, it is above the hexagonal facet of the C_{60} molecule. As the temperature is decreased, the number of pairs of molecules in the first orientation increases and reaches 83% at 90 K. Below 90 K, the ratio of molecules in the first and second orientations remains constant, but ratchet rotation of the C_{60} molecules occurs in such a manner that each of two orientations is transformed only to the equivalent one.[25] This results in ordering, in which the rotation of the C_{60} molecules in a crystal is synchronised completely. This kind of ordering can also occur in D–A complexes and radical ionic salts of fullerenes provided that the distances between the C_{60} molecules are short.[38–40]

4. Conducting and magnetic properties of fullerenes

The upper unoccupied and lower occupied levels of the C_{60} molecule are presented in Fig. 1. The highest occupied h_u level is five times degenerate and is completely filled with ten electrons. The lowest free t_{1u} and t_{1g} levels are three times degenerate.[25, 36]

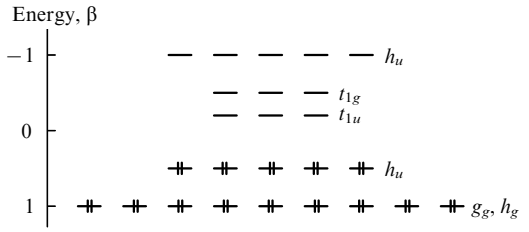


Figure 1. Highest occupied and lowest unoccupied molecular π-orbitals of the C_{60} fullerene calculated by the Hückel method;[36] β is resonance integral.

Overlapping of π-orbitals of the adjacent C_{60} molecules in a crystal results in the formation of a valence band and a conduction band. The energy gap between the valence band and the conduction band in C_{60} is estimated as 1.5–1.8 eV,[25, 36] hence crystalline fullerene is a semiconductor. The highest-energy edge of the valence band consists of the h_u levels, while the lowest-energy edge of the conduction band consists of the t_{1u} levels (see Fig. 1).

Magnetic measurements carried out with pure C_{60} and C_{70} fullerene specimens have shown that magnetic transitions are observed at 60 K.[40] This is due to the fact that the currents of π-electrons in the six- and five-membered fullerene rings are different and create a very small but distinct magnetic moment in the fullerene molecule [for C_{60}, $\mu = -0.35 \times 10^{-9}$ A m^2 (see Ref. 27)]. Cooling of specimens of pure C_{60} below 90 K results in the transition to ratchet synchronised rotation of the fullerene molecules. In this transition, the positions of 83% of the magnetic moments of the C_{60} molecules are frozen in an ordered fashion, but 17% of the magnetic moments are frozen in disorder. This results in a glassy magnetic state.[40]

When C_{60} specimens are placed in a magnetic field, the magnetic moments of the C_{60} fullerene molecules are oriented along the external magnetic field. Therefore, cooling of C_{60} specimens in a magnetic field below the temperature of transition to synchronised rotation of fullerene molecules results in freezing of the ordered positions of the magnetic moments of the C_{60} molecules and formation of the frozen glassy magnetic state. Heating of the specimens above the temperature of this transition results in violation of the synchronised rotation of fullerene molecules, and ordering of the magnetic moments of the C_{60} molecules disappears.[40]

III. Donor – acceptor complexes and radical ionic salts of fullerenes

1. Methods of preparation

Fullerene compounds are prepared using various methods: slow concentration of solutions,[41–43] diffusion methods,[44–52] cooling of saturated solutions,[53, 54] precipitation with a solvent[48–50, 55] and an electrochemical method.[56–61]

Concentration of solutions containing a fullerene and a donor is the basic method for the preparation of molecular fullerene complexes. The concentration is carried out in an inert atmosphere, as molecular oxygen can be absorbed on the surface of the fullerene molecule, which blocks the approach of the donor to the fullerene.[62]

As a rule, those solvents are used in which fullerenes are well soluble: carbon disulfide (7.9 mg ml^{-1}), benzene (1.5 mg ml^{-1}), toluene (2.9 mg ml^{-1}) and chlorobenzene (5.7 mg ml^{-1}).[63, 64] Fullerene forms solvates of the type $C_{60}(Sol)_x$ with many of these solvents.[65–74]

Two competing reactions occur upon concentration in a reaction system 'donor – C_{60} – solvent':

$$C_{60} + Sol + D \longrightarrow \begin{cases} \rightarrow D_n(C_{60})_m(Sol)_l \\ \rightarrow C_{60}(Sol)_x \end{cases}$$

Sol is a solvent, D is a donor;
$n = 1–6$, $m = 1–3$, $l = 0–4$; $x = 0.4–4$.

Shifting of the reaction equilibrium towards the formation of a complex (as the solvent is present in a considerable excess in comparison with the donor) sometimes requires a great molar excess of the donor relative to the fullerene (up to 100 : 1).[75–77] As the temperature is increased, the rate of displacement of the solvent by the donor from the solvent shell increases, thus the time of heating or refluxing of the reaction mixture is an essential factor. An increase in the temperature of concentration of fullerene solutions in benzene results in a decrease in the content of benzene in the crystal solvate [$C_{60} – C_6H_6$], and above 40 °C the solvate is decomposed completely and virtually pure fullerene is formed.[42]

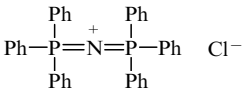
To avoid losses on the walls of the reaction vessel in the preparation of microquantities of complexes, special techniques for the concentration of the solvent in closed volume using a temperature gradient have been developed.[41, 42]

Fullerene compounds can be isolated from solutions by precipitation or cooling of saturated solutions. For example, radical anionic salts of fullerenes are isolated from solutions in pyridine and benzonitrile by precipitation with non-polar solvents (pentane or hexane). However, this results in polycrystalline specimens.[48–50, 55] Single crystals of the $K_3C_{60}(THF)_{14}$ salt can be prepared by slow gradient cooling of a solution obtained by treatment of the C_{60} fullerene with potassium in tetramethylethylenediamine in the presence of tetrahydrofuran and diethyl ether.[53]

The diffusion method (in which the vessels with solutions of a fullerene and an appropriate donor are connected by a tube filled with a solvent) is most suitable for the preparation of single crystals of poorly soluble C_{60} compounds. Single crystals of the

complexes (DAN)$C_{60}(C_6H_6)_3$ (DAN is dianthracene),[44] the salt (TDAE)C_{60} [TDAE is tetrakis(dimethylamino)ethylene][45,46] and others have been obtained using this procedure.[47]

The diffusion method is also used in the synthesis of fullerene radical anionic salts by cationic metathesis. The reaction is carried out in two stages. In the first stage, C_{60} is reduced with an excess of sodium in THF in the presence of dibenzo-18-crown-6[48–50] or other crown ethers.[51] The degree of reduction of the fullerene to the $C_{60}^{n-\bullet}$ anion is controlled by the exact molar ratio of the fullerene and the crown ether ($1:n$). The salt $[Na^+(18\text{-crown-}6)]C_{60}^{-\bullet}(THF)_3$ is isolated from THF by precipitation with hexane.[49] Similar C_{60}^{2-}, $C_{60}^{3-\bullet}$ and C_{60}^{4-} salts are poorly soluble in THF and spontaneously precipitate from solutions.[49,51] In the second stage, the resulting sodium salts of C_{60} are dissolved in acetonitrile and placed in a vessel. A compound with a bulky cation, for example, bis(triphenylphosphoranylidene)ammonium chloride **5** (PPNCl), is placed in the other vessel.[50,51]



5

The vessels are connected by a tube containing the pure solvent. Single crystals of $(PPN)_2C_{60}$ have been obtained by this method.[50] Cationic metathesis of Rb_3C_{60} with the salts Me_4NCl, Et_4NBr and Me_4PCl in liquid ammonia can also be used; the specimens were isolated as powders.[52]

In the electrochemical method, the radical anions $C_{60}^{-\bullet}$ and $C_{70}^{-\bullet}$ were obtained by reduction of neutral fullerenes in an H-shaped cell on a platinum cathode. Compounds Ph_4PCl or PPNCl with bulky cations were used as the supporting electrolytes.[56–60] 1,2-Dichlorobenzene or mixtures of dichloromethane with toluene and chlorobenzene with tetrahydrofuran served as the solvents. The fullerene salts crystallised on the cathode.[56–60]

The salts $M_xC_{60}(THF)_y$ with alkali metals (M = Li, Na, K, $x \sim 0.4$, $y \sim 2.2$) were obtained by electrochemical reduction of C_{60} in the presence of a supporting electrolyte, *viz*., the corresponding tetraphenylborate. A mixture of chlorobenzene with THF served as the solvent.[61]

2. Solvate and clathrate compounds. Inclusion compounds

Dissolution of C_{60} in various solvents results in formation of donor–acceptor compounds.[65,66] The interaction of the solvent with C_{60} occurs basically through polarisation van der Waals forces. In fact, the solubility of fullerenes in solvents with high polarisability, especially in benzene ($\alpha \sim 10$ Å^3) and naphthalene derivatives ($\alpha \sim 20$ Å^3) is the highest.[63,64] Most of the complexes with solvents are unstable, but in some cases C_{60} solvates can be isolated as crystals by slow concentration of the solutions.[67–74]

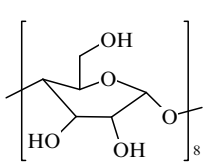
The interaction with the solvent molecules results in the orientational ordering of molecules compared to crystalline C_{60}; in certain cases, this allows one to perform X-ray diffraction studies of these compounds. Solvate compounds have diverse crystal structures: $C_{60}(C_6H_6)CH_2I_2$ has lamellar packing,[67] $C_{60}(C_6H_6)_4$ forms a cage with hexagonal channels,[68,69] while $C_{60}(C_6H_{12})_2$[70] and $C_{60}(1,2\text{-}Me_2C_6H_4)_2$[71] have hexagonal layered packing. The crystal cells of the solvates have lower symmetry than that of pure C_{60}. However, the crystal structure could not be determined for many solvates, such as $C_{60}(Cl_2C{=}CHCl)$,[72] $C_{60}(CS_2)$[73] and $C_{60}(CCl_4)_{10}$,[74] because of significant orientational and structural disorder.

The solvent molecules in clathrate compounds are located in the cavities between the bulky fullerene molecules. Clathrate compounds of C_{60} are obtained by precipitation of the fullerene from toluene with a large excess of the other solvent, *viz*., *n*-pentane, 1,3-dibromopropane, butanone, diethyl ether, acetone,[78] n-heptane,[79] *etc*.[80,81] The composition of the clathrates is $C_{60}(Sol)_x$. For solvents with small molecules, $x = 1$. As the size of solvent molecules increases, x decreases. Precipitation of fullerene with isobutane results in pure C_{60}.[78] Clathrate compounds have been obtained basically with the solvents in which the solubility of fullerene is very small; this suggests that the interaction between the molecules of the solvent and fullerene is weak.[78–81]

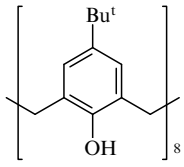
Solvate and clathrate compounds are characterised by phase transitions related to orientational ordering of the fullerene molecule. For instance, phase transitions for $C_{60}(Me_2CO)$ occur at 240 K,[78] for $C_{60}(CS_2)_x$ at 230 K,[78] for $(TSeT)_xC_{60}(CS_2)_y$ (TSeT is tetraselenatetracene) at 203–240 K,[82] for $C_{60}(C_5H_{12})$ at 190 K,[78] for $C_{60}[Br(CH_2)_3Br]$ at 190 K[78] and for $C_{60}(Cl_2C{=}CHCl)$, at 167 K.[72] All these transitions are similar to the phase transition in pure C_{60} at 255 K.[37]

Compound $(TSeT)_xC_{60}(CS_2)_y$ contains up to 26% of carbon disulfide and only traces of the donor.[82] The high content of the solvent probably results in orientational disorder and separates the C_{60} molecules from each other to such an extent that upon complete removal of carbon disulfide the fullerene is completely sublimed at ~520 °C, whereas the maximum sublimation rate of pure C_{60} is reached only at 700 °C.[82]

Inclusion compounds of fullerenes are obtained by refluxing aqueous solutions of γ-cyclodextrin **6** (γ-CD) with finely dispersed fullerene.[83–85] There are two types of complexes of γ-CD with C_{60}: one C_{60} molecule forms van der Waals contacts with two γ-CD molecules, or a van der Waals aggregate of several C_{60} molecules forms short contacts with several γ-CD molecules.[83–85] The unique property of these compounds is their solubility in water, therefore such complexes can be utilised in reactions that occur in the presence of water. In particular, complexes of fullerene with γ-CD can be used for medical purposes.[95] Similar compounds are formed upon dissolution of a mixture of fullerenes with *p-tert*-butylcalix[8]arene (**7**) in toluene.[86] Complexation with calixarenes has been proposed for efficient separation of fullerene mixtures.[86,87] It is possible to isolate C_{60} of 99.5% purity by multiple recrystallisation of a mixture containing 85% C_{60} and 15% C_{70}.[86] It was shown that fullerene molecules are separated from each other in crystal structures of compounds C_{60}–*p*-iodocalix[4]arene[88] and C_{60}–*p*-iodocalix[5]arene.[89]



6

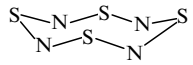


7

3. Complexes with inorganic compounds

Complexes of fullerenes with S_8,[41,90–92] P_4,[93] I_2,[94] S_4N_4[75,95] and a number of other small molecules have the composition $C_{60}X_2$ or $C_{60}X(Sol)$. The crown-shaped S_8 molecule is very flexible, and molecular sulfur readily forms complexes with fullerenes. The structures of compounds $C_{60}(S_8)_2$ and $C_{60}S_8(CS_2)$ are cage lattices of the fullerene molecules with channels filled with the sulfur molecules.[90,91] In compounds $C_{70}(S_8)_6$ and $C_{76}(S_8)_6$, the fullerene molecules form loose corrugated hexagonal layers with distances between the fullerene molecules 10.2–10.5 Å.[41,92] All S_8–fullerene compounds contain shortened S–C contacts [3.13–3.52 Å, which is shorter than the sum of the van der Waals radii of sulfur and carbon (3.7 Å)]. As a result of this strong interaction, the rotation of fullerene molecules ceases almost completely. This made it possible to establish the structure of the fullerenes C_{70} (see Ref. 92) and C_{76} (see Ref. 36) more precisely. The complex $C_{60}(P_4)_2$ has a laminar structure.[93] In compound $C_{60}I_2(C_6H_5Me)$, iodine can act as an acceptor with respect to C_{60}, as its EA (3.06 eV) is higher than that of fullerene (2.65 eV). This compound has a donor–acceptor sandwich structure, in which the iodine molecules are located between the fullerene and toluene molecules.[94]

Tetrasulfur tetranitride S_4N_4 (**8**), like S_8, has a crown shape and forms a number of molecular complexes with the C_{60} fullerene.



8

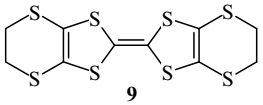
The following compounds were isolated from toluene: $C_{60}\cdot S_4N_4$ and $C_{60}(S_4N_4)_2$.[75] The similarity of the sizes of the S_4N_4 and benzene molecules results in their mutual replacements in the crystal lattice of the complex. For this reason, compounds of the series $C_{60}(S_4N_4)_{2-x}(C_6H_6)_x$ were isolated from benzene, where $x < 2$.[75,95] This replacement has a random character, and the use of an excess of the donor yields compounds with a higher content of S_4N_4. In the crystal structure of the complex $C_{60}(S_4N_4)_{1.33}(C_6H_6)_{0.67}$, the densely packed layers of fullerene molecules alternate with layers of tetrasulfur tetranitride and benzene molecules.[95]

The Pd_6Cl_{12} cluster and C_{60} form a complex $C_{60}(Pd_6Cl_{12})_2(C_6H_6)_3$ with cage structure, in which each fullerene molecule is surrounded by eight Pd_6Cl_{12} molecules.[96]

4. Complexes with organic donors

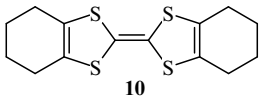
The interest in complexes of fullerenes with donors of the tetrachalcogenafulvalene class (**9**–**17**) is primarily related to the fact that both tetrathiafulvalene and its derivatives are the main components in the production of organic metals and superconductors.[10]

It is known[97] that tetrachalcogenafulvalenes are strong donors with IPs ranging from 6.3 to 7.4 eV. The molecular polarisability of these donors is 15–38 Å.[97] Tetrathiafulvalenes have planar structures, sometimes with a small deviation of the terminal groups from the conjugation plane.[10] This structure allows arrangement of their salts in regular stacks or layers. A partial charge transfer ($0.25 \leqslant \delta \leqslant 1$) from the donor to the acceptor is a prerequisite for the appearance of conductivity.[8] Tetrathia(selena,tellura)fulvalenes **9**–**17** are widely used as donors for the preparation of complexes with fullerenes.



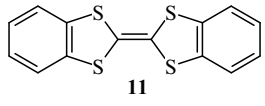
9

(BEDT–TTF)



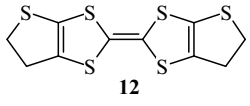
10

(OM–TTF)



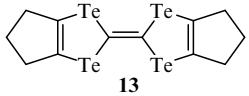
11

(DB–TTF)



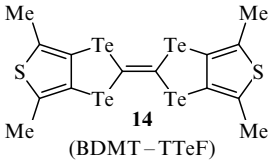
12

(BET–TTF)



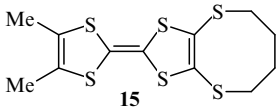
13

(HM–TTeF)



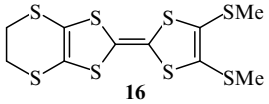
14

(BDMT–TTeF)



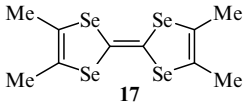
15

(TMDTDM–TTF)



16

(C_1TET–TTF)



17

(TM–TSeF)

The $(BEDT–TTF)_2C_{60}$ complex was the first to be obtained.[98] Subsequently, about a dozen compounds of fullerenes with tetrachalcogenafulvalene derivatives have been synthesised (Table 2). It was found that the degree of charge transfer in these compounds is insignificant.[5,98,103–106] This is due both to the weak acceptor properties of fullerene and the steric factors unfavourable for charge transfer from the π-orbitals of the initially flat donors to the spherical t_{1u} orbital of C_{60}.[106] The formation of complexes with spherical fullerene molecules results in strong distortion of the flat tetrachalcogenafulvalene molecules, which assume boat conformations: the dihedral angles between the flat central fragment E_4C_2 and the terminal groups of tetrachalcogenafulvalene derivatives are 20–30°,[98,101,103,105,107] which results in some violation of π-conjugation in these molecules.[108]

The packing of fullerene molecules in the crystals of these complexes can be diverse: dense[5,89,100] or rather loose[107,108] layers of C_{60} molecules,[98,100] double chains of C_{60} molecules[98,102,110] as well as island motifs with isolated C_{60} mole-

Table 2. Fullerene complexes with tetrachalcogenafulvalenes.

Donor	Abbreviation	Solvent	Donor : fullerene : solvent ratio	Structural type	Ref.
Bis(ethylenedithio)tetrathiafulvalene	BEDT–TTF (**9**)	without solvent	2 : 1	chain	98, 99
Octamethylenetetrathiafulvalene	OM–TTF (**10**)	C_6H_6	1 : 1 : 1	layered	5
Dibenzotetrathiafulvalene	DB–TTF (**11**)	C_6H_6	1 : 1 : 1	island	100
		C_5H_5N	1 : 1 : 1	—	100
		C_6H_6	1 : 1 : 1 [a]	—	100
Bis(ethylenethio)tetrathiafulvalene	BET–TTF (**12**)	C_6H_5Me	1 : 1 : 1	layered	101
		C_6H_5Cl	1 : 1 : 1	"	101
Hexamethylenetetratellurafulvalene	HM–TTeF (**13**)	without solvent	1 : 1	"	102
Bis(dimethylthieno)tetratellurafulvalene	BDM–TTeF (**14**)	CS_2	1 : 1 : 1	island	103
Tetramethylenedithiodimethyltetrathiafulvalene	TMDTDM–TTF (**15**)	CS_2	2 : 1 : 3	layered	104, 105
Bis(methylthio)ethylenedithiotetrathiafulvalene	C_1TET–TTF (**16**)	without solvent	2 : 1	double chains	106
Tetramethyltetraselenafulvalene	TM–TSeF (**17**)	CS_2	1 : 1 : 2	layered	107
		C_6H_6	1 : 1 : 0.5	"	102

[a] For the C_{70} fullerene.

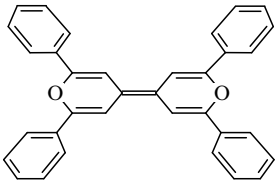
Table 3. Complexes of C_{60} with organic donors.

Donor	Abbreviation	Solvent	Donor : fullerene : solvent ratio	Structural type	Ref.
2,2′,6,6′-Tetraphenyldipyranylidene	TPDP (**18**)	CS_2	1 : 2 : 4	layered	43, 109
3,3′,4,4′-Tetrathiabis(1,2,5-thiadiazole)	*twin*-TDAS (**19**)	without solvent	4 : 3	cage	113
Bis(ethylenedithiotetrathiafulvaleno)[*b*,*h*]-1,4,7,10-tetrathiacyclododeca-2,8-diene	*twin*-BEDT – TTF (**20**)	CS_2	1 : 1 : 1	chain	110
Cyclotriveratrylene	CTV (**21**)	C_6H_5Me	1 : 3 : 1	island	114
9,9′-*trans*-Bi(telluraxanthenyl)	BTX (**22**)	CS_2	1 : 1 : 1	"	54, 111
(9,10,9′,10′)-Bi(9,10-dihydroanthrylene) (dianthracene)	DAN (**23**)	C_6H_6	1 : 1 : 3	layered	44
2,3,6,7,10,11-Hexamethoxytriphenylene	HMT (**24**)	without solvent	2 : 1	island	115
$SbPh_3$		the same	6 : 1	"	116
$Au(PPh_3)Cl$		"	2 : 1	"	117
Hydroquinone		"	3 : 1	"	118

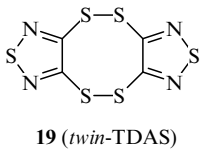
cules.[101, 105, 111] The donor-acceptor interaction of tetrathiafulvalene molecules with C_{60} occurs both by the $n-\pi$ type (the *n*-orbitals of the sulfur atom of the central E_4C_2 donor fragment are directed to the centre of the six-membered ring of one C_{60} molecule) and by the $\pi-\pi$ type (the central E_4C_2 donor fragment is almost parallel to the six-membered ring of the other C_{60} molecule).[98, 105] The distance between heteroatoms of the donor and atoms of the C_{60} molecule is somewhat shorter than the sum of the van der Waals radii of the corresponding heteroatoms and carbon atoms.[98 – 107]

Syntheses of tetrathiafulvalene complexes with halogenated fullerenes have been described. As halogenated fullerenes are stronger acceptors than the C_{60} fullerene, the oxidation of tetrathiafulvalenes with the formation of radical cationic salts is possible.[33, 119]

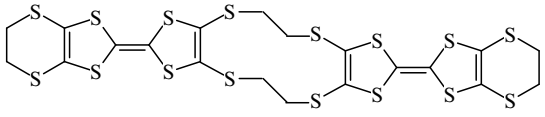
In addition to compounds of fullerenes with tetrachalcogenafulvalene derivatives, compounds with donor molecules of other classes (Table 3) have also been obtained.



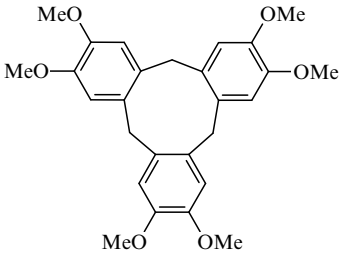
18 (TPDP)



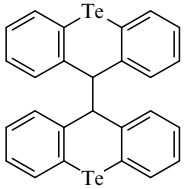
19 (*twin*-TDAS)



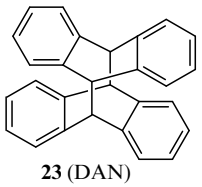
20 (*twin*-BEDT – TTF)



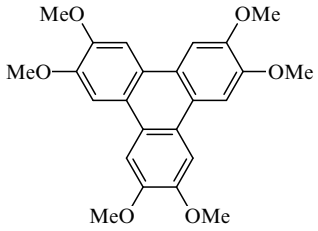
21 (CTV)



22 (BTX)



23 (DAN)



24 (HMT)

The molecules of compounds **21** (CTV),[114] **22** (BTX)[54, 111] and **23** (DAN)[44] have three-dimensional shapes (BTX and DAN, of the 'double butterfly' type, and CTV, of the hemisphere type). The structures of these molecules match well the spherical surface of the C_{60} molecule, which forms molecular complexes with them owing to numerous van der Waals contacts. DAN has a unique ability to undergo cocrystallisation with C_{60} almost quantitatively even from dilute solutions in benzene; this can be utilised for the isolation of C_{60} from various mixtures.[44] The C_{70} fullerene matches less the spatial shape of such molecules as CTV and DAN and does not form complexes with these donors.[44, 114] However, it forms complexes with composition 1 : 1 : 0.5 with BTX and CS_2.[119] Isolated packing of C_{60} molecules is characteristic of complexes with other donors, such as HMT,[115] $SbPh_3$,[116] $Au(PPh_3)Cl$[117] and hydroquinone[118] (see Table 3).

All of the complexes described above are dielectrics with a conductivity of $\sim 10^{-6}$ S cm^{-1} and less.[5, 100, 103, 104]

5. Composites of conducting polymers with the C_{60} fullerene

The discovery of the photoinduced charge transfer in polyvinylcarbazole – C_{60} composites[17] stimulated the intense development of studies in this field. Composites with a dozen of different polymers have been studied by now.[120] Films of polymer – C_{60} composites are prepared by concentration of solutions of a polymer and a small amount of a fullerene (from 1% to 3% of the polymer weight) in aromatic hydrocarbons on a substrate.[17, 120 – 122]

Only weak charge transfer from the polymer to the fullerene is observed in these composites in the ground state.[121,122] For example, an ESR signal corresponding to an insignificant concentration of $C_{60}^{-\bullet}$ (2.3×10^{18} spins g^{-1}) was detected in a composite polyvinylpyrrolidone – C_{60}.[122]

The polymer photoexcitation occurs at energies higher than the difference between the HOMO and LUMO levels of the polymer. This is accompanied by fast transfer of an electron

($< 10^{-12}$ s) from the photoexcited polymer molecule to the C_{60} molecule with formation of a complex (polymer$^+$)–$C_{60}^{-\bullet}$ in excited state. Transition to the state with free separate charge carriers is now possible from this state.[121] Charge separation in the excited state of CTC results in the generation of charge carriers and a strong increase in the photoconductivity of the polymer.[121]

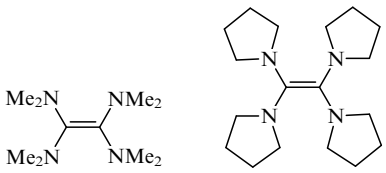
The involvement of a fullerene in efficient charge separation in these composites is reduced to two factors. On the one hand, as an acceptor, the fullerene accepts electrons occupying the LUMO of the polymer upon photoexcitation with formation of vacancies ('holes') on the polymer. On the other hand, the recombination of photoexcited electrons and 'holes' is considerably inhibited due to their spatial separation upon delocalisation of charges on the bulky fullerene molecule.[121] As the rate of electron transfer is high and the rate of carrier recombination is relatively low, the quantum yield of formation of charge carriers increases considerably in the presence of a fullerene.[121, 122]

The possibility of using these composites in xerography, in solar energy phototransducers and in other devices is being studied.[120, 121]

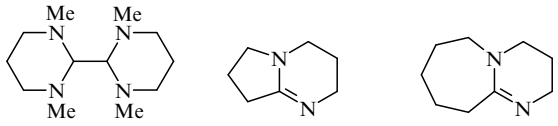
6. Complexes and radical ionic salts of fullerenes with amines. Magnetic properties of the (TDAE)C_{60} salt

The detection of ferromagnetic transition with the highest temperature known for organic materials (Table 4)[15] in the salt formed by the C_{60} fullerene and tetrakis(dimethylamino)ethylene (**25**) (TDAE)C_{60} has stimulated strong interest in compounds of C_{60} with amines. Polycrystalline specimens of fullerene compounds with amines are obtained by precipitation of a fullerene solution in toluene with an excess of amine.[15, 123–128] Single crystals of (TDAE)C_{60} have been obtained by mutual diffusion of solutions of tetrakis(dimethylamino)ethylene **25** and C_{60} in toluene.[45, 46] Other unsaturated amines, *e.g.*, **26** and **27**, react with fullerenes to give radical anionic salts having unusual magnetic properties (see Table 4).[123–128]

Saturated amines, such as *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) or triphenylamine (TPA) (see Table 4), possess weaker donor properties than the amine **25**, and form only weak charge-transfer complexes.[76, 77, 129] These compounds are obtained by concentrating solutions of fullerenes in chlorobenzene with a large excess of the donor (100 : 1). The existence of charge transfer in compounds of C_{60} with TMPD is confirmed by the presence of an absorption band of $C_{60}^{-\bullet}$ at 1070 nm in the optical spectrum and a shift of the absorption band of the $T_{1u}(4)$ vibration of C_{60}, which is sensitive to charge transfer onto the fullerene molecule, in the IR spectrum.[76]



25 **26** **27**



28 **29** **30**

Amines with sterically unhindered nitrogen atoms add to fullerenes.[132] Some amines with strong donor properties, such as **27**, **29** or **30**, reduce fullerene and add to it. The reaction of C_{60} with these amines in solution[123, 127, 128] can occur in two steps:

$$\mathrm{Am} + [C_{60}] \xrightarrow{k_1} \underset{\text{salt}}{[\mathrm{Am}^+][C_{60}^{-\bullet}]} \xrightarrow{k_2} \underset{\text{zwitter-ion}}{[\mathrm{Am}^+C_{60}^{-\bullet}]}$$

Am is an amine.

If the first reaction step is sufficiently fast (k_1 is high) and the resulting salt is poorly soluble in the solvent (as in the case of TDAE), the reaction stops in the first step, and the salts $[Am^+][C_{60}^{-\bullet}]$ can be isolated. If k_1 is small and the formation of salts occurs slowly (as in the case of amines **29**, and, especially, **27** and **30**), and the resulting salts are rather soluble in the solvent, the amine adds to C_{60} in this stage to give diamagnetic zwitterions.[123, 127, 128] These reactions are accompanied by recombination of radicals, which results in a gradual decrease in the signal of the radical anion $C_{60}^{-\bullet}$. The addition products that are precipitated from the solution contain a small amount of the radical anion $C_{60}^{-\bullet}$ [4% and 2% for (DBU)C_{60} and (TMBI)C_{60}, respectively[123, 128]]. Fullerene mixed addition and reduction products are perhaps formed in the reaction. If the salt is rapidly precipitated from benzene, the addition cannot go to completion. In this case, the reaction product, *viz.*, (DBN)C_{60}, contains a large percentage of reduced $C_{60}^{-\bullet}$ (14%) and manifests strong magnetic fluctuations down to 80 K.[127] The addition of amines to C_{60} complicates the study of these compounds and results in significant differences in the estimation of their magnetic properties.

The compound (TDAE)C_{60} has been studied by IR,[133] Raman,[134] ESR,[135–137] NMR[138] and X-ray photoelectron[139] spectroscopies. The temperature of ferromagnetic transition in (TDAE)C_{60} is 16.1 K. It has been shown[39, 43, 135] that the onset of

Table 4. Donor-acceptor complexes and radical ionic salts of C_{60} with amines.

Donor	Abbreviation	D : C_{60} ratio	Compound type	S[a]	Magnetic properties	Ref.
Tetrakis(dimethylamino)ethylene	TDAE (**25**)	1 : 1	salt	1	ferromagnetic (T_c = 16.1 K)	15
Tetrakis(pyrrolidino)ethylene	TPYE (**26**)		–		superposition of paramagnetic and ferromagnetic phases	125
2,2-Bi(1,3-dimethylimidazolidin-2-ylidene)	TMBI (**27**)	1 : 1	CTC see note[b]	0.02	weak paramagnetic ferromagnetic (T_c < 140 K)	123 124
2,2′-Bi(1,3-dimethylhexahydropyrimidin-2-yl)	TMBH (**28**)	–	–		antiferromagnetic	126
1,5-Diazabicyclo[4.3.0]non-5-ene	DBN (**29**)	2 : 1	CTC[b]	0.14	weak antiferromagnetic	127
1,8-Diazabicyclo[5.4.0]undec-7-ene	DBU (**30**)	2 : 1	CTC[b]	0.04	only near magnetic order observed	128
N,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine	TMPD	1 : 1	CTC		–	76, 129
Triphenylamine	TPA	1 : 1	molecular complex		–	77
1,5-Diaminopentane	DAP	3 : 1	–		–	130, 131

[a] Number of spins per formula unit determined by ESR; [b] addition of amine to fullerene is possible.

the ferromagnetic state in (TDAE)C_{60} specimens requires that they were kept for several days at 20–100 °C (constant temperature). Without this procedure, the (TDAE)C_{60} specimens manifest only antiferromagnetic properties.[39, 43, 135]

Several mechanisms for the origin of the ferromagnetic state in (TDAE)C_{60} have been discussed.[38, 140, 141] It has been shown by ESR [137, 142] that in (TDAE)C_{60} complete charge transfer from the donor to the fullerene occurs. It was assumed that ferromagnetism is due to the presence of the radical anion $C_{60}^{-\bullet}$. However, other salts with the radical anion $C_{60}^{-\bullet}$ do not manifest any ferromagnetism.[38, 141]

It was suggested [38, 39] that ferromagnetism in (TDAE)C_{60} is also determined by the presence of the radical cation $TDAE^{+\bullet}$. The ESR spectrum of (TDAE)C_{60} contains only one line with $g = 2.0008$, which is an average value between those for $TDAE^{+\bullet}$ ($g = 2.0035$) and $C_{60}^{-\bullet}$ ($g = 1.9960$).[38, 142] This is probably due to the strong exchange interaction between $TDAE^{+\bullet}$ and $C_{60}^{-\bullet}$. The C_{60} molecules in crystalline (TDAE)C_{60} are packed in one-dimensional chains along the crystallographic axis $\bar{c}$ with shortened distances between the centres (9.98 Å)[15, 45] (Fig. 2). The presence of shortened contacts between the C_{60} molecules allows the slowing down of the rotation of these molecules on cooling, with transition to synchronised ratchet rotation, as in crystals of pure C_{60} cooled below 90 K. In fact, the rotation of the C_{60} fullerene molecules in (TDAE)C_{60} slows down at temperatures below 150 K, as confirmed by broadening of the ^{13}C NMR signal.[38, 138] According to theoretical calculations, the negative charge of the radical anion $C_{60}^{-\bullet}$ is mostly concentrated in the equatorial area of the fullerene sphere. Because of this, long-range magnetic order can be formed in this salt upon transition to synchronised rotation of C_{60} molecules.[38, 39] In this case, the spins of $C_{60}^{-\bullet}$ in the fullerene chain along the crystallographic axis $\bar{c}$ are ordered antiferromagnetically. The antiferromagnetic interaction can be transferred between the fullerene chains through the radical cation $TDAE^{+\bullet}$ (see Refs 38 and 39).

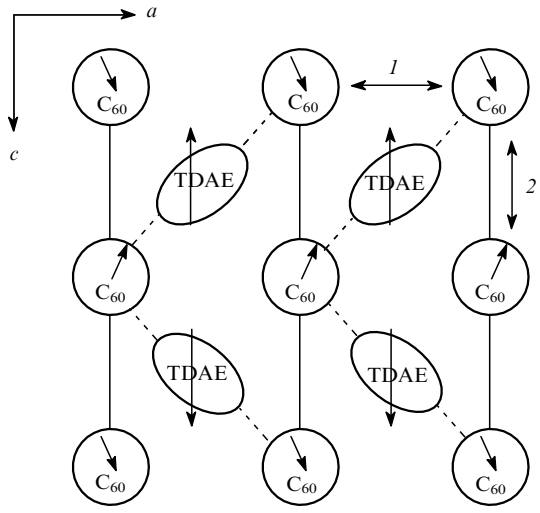


Figure 2. Scheme for formation of ferromagnetic order in the salt (TDAE)C_{60} by the spin polarisation mechanism;[38, 39]
(*1*) is ferromagnetic interaction; (*2*) is antiferromagnetic interaction.

According to theory,[39] distortion of the radical cation $TDAE^{+\bullet}$ may result in inhomogeneous spin density distribution on $TDAE^{+\bullet}$ (Fig. 2). In fact, after keeping of the salt (TDAE)C_{60} at constant temperature,[39] the ^1H NMR spectrum displays two sets of lines (A and B) from the methyl groups of $TDAE^{+\bullet}$ (see Ref. 138). This implies an asymmetrical spin density distribution in the radical cation $TDAE^{+\bullet}$. Asymmetrical spin density distribution results in violation of the antiferromagnetic order of the $C_{60}^{-\bullet}$ spins (Fig. 2) and the onset of ferromagnetic transition below 16.1 K. Ferromagnetic ordering of the $C_{60}^{-\bullet}$ spins is observed in the plane *ab* normal to the crystallographic axis $\bar{c}$ (Fig. 2).

Compound (TDAE)C_{60} manifests only antiferromagnetic properties without preliminary keeping at constant temperature. In this case, the spin density is uniformly distributed on $TDAE^{+\bullet}$, and the intensity ratio of lines A and B in the ^1H NMR spectrum of (TDAE)C_{60} differs from that of the specimens kept at constant temperature.[39,138]

No ferromagnetic properties have been found for compounds of TDAE with higher fullerenes (C_{70}–C_{96}). This is apparently due to differences in the electronic structures of $C_{60}^{-\bullet}$ and radical anions of higher fullerenes, as the negative charge in the mono-anions of higher fullerenes was found to be delocalised over the entire anion surface rather than in the equatorial area of the sphere, as is the case in $C_{60}^{-\bullet}$ (see Ref. 143).

The conducting properties of some compounds of fullerenes with amines have been studied.[45, 46, 123] The antiferromagnetic phase of the salt (TDAE)C_{60} displays semiconductor properties with a conductivity of about 10^{-5} S cm^{-1} and an activation energy (E_a) of 0.4–0.8 eV.[46] The conductivity of the ferromagnetic phase of (TDAE)C_{60} at room temperature is of the same order of magnitude (5×10^{-5} S cm^{-1}). It is also of activated character and is due to tunnelling of electrons between the fullerene molecules. Electron transfer is largely affected by the rotation of fullerene molecules; for this reason, the decrease in the activation energy at 150 K from 0.3 to 0.14 eV is explained by slowing down of the rotation of C_{60} molecules in this salt.[45] It was shown [123] that the conductivity of (TMBI)C_{60} is 5×10^{-4} S cm^{-1}.

Measurements on a SQUID magnetometer have shown that a superconducting phase with $T_c = 17.4$ K may be present in (TDAE)C_{60}.[16] The volume of the superconducting phase increases if the sample is cooled very slowly at ~150 K, which temperature corresponds to the transition to hindered and synchronised rotation of the C_{60} molecules.

7. Complexes and radical ionic salts of C_{60} with metallocenes

Table 5 lists the compounds of C_{60} with metallocenes. The donor properties of metallocenes vary over a wide range, and they can form compounds with different degrees of charge transfer with fullerenes (from molecular complexes to radical ionic salts containing $C_{60}^{3-\bullet}$).[50, 151] The cyclopentadienyl rings of metallocenes coordinated with fullerenes are parallel to the five-membered fullerene rings. For example, the deviation from this plane in the structure $[(C_5Me_5)_2Ni]C_{60}(CS_2)$ is only 0.3° (see Ref. 149). Such a coordination ensures the maximum overlapping of the metallocene and fullerene π-orbitals and efficient charge transfer.

Two types of structures are characteristic of compounds of metallocenes with fullerenes. In compounds of C_{60} with ferrocene and cobaltocene, dense layers of fullerene molecules alternate with layers of the metallocene molecules.[47, 145] The layers of the fullerene molecules in compounds with substituted metallocenes are looser and also alternate with the layers of the donor.[149] The physical properties of these compounds are little studied. It is known that the ESR spectra of compounds of C_{60} with nickelocene and decamethylferrocene contain a signal corresponding to $C_{60}^{-\bullet}$ (see Ref. 147). The complexes $[(C_5H_5)_2Ni]C_{60}$ and $[(C_5H_5)_2Co]C_{60}$ display magnetic properties with an S-shaped magnetisation curve which has a hysteresis. However, these properties disappear on exposure of the specimens to air,[140] which indicates that the radical anions $C_{60}^{-\bullet}$ in these complexes are sensitive to oxygen. It has been shown that the conductivity of $[(C_5Me_5)_2Ni]C_{60}(CS_2)$ is rather high (10^{-2} S cm^{-1}).[149]

8. Fullerene salts with bulky cations

Radical anionic salts of $C_{60}^{-\bullet}$ and $C_{70}^{-\bullet}$ with bulky cations, such as Ph_4P^+, PPN^+ and others,[56–58, 152–154] are stable in air (Table 6). Each radical anion of C_{60} in these ionic compounds is located in a highly symmetrical cationic environment. The phenyl substituents

Table 5. Compounds of C_{60} fullerene with metallocenes.

Donor	Solvent	D : C_{60} : Sol ratio	Compound type	Magnetic properties	Ref.
$(C_5H_5)_4Fe_4(CO)_4$	C_6H_6	1 : 1 : 0.3	molecular complex	–	144
$(C_5H_5)_2Fe$	without solvent	2 : 1	the same	–	145
$(C_5Me_5)_2Fe$	the same	2 : 1	CTC [a, b]		146
Biferrocenyl	MeCN	0.8 : 1 : 0.7	CTC	superposition of paramagnetic and ferromagnetic phases	147
$(C_5H_5)_2Ni$	without solvent	1 : 1	CTC [a, b]	displays magnetic properties [b]	146
$(C_5Me_5)_2Mn$	the same	1 : 2	CTC		148
$(C_5Me_5)_2Ni$	CS_2	1 : 1 : 1	CTC [a]	$\sigma = 10^{-2}$ S cm^{-1}	149
$(C_5H_5)_2Co$	PhCN	1 : 1 : 1		displays magnetic properties [b]	48
	CS_2	1 : 1 : 1	CTC [a, b]	the same	47
$(C_6H_6)_2Cr$	without solvent	1 : 1	CTC		150
$(C_5Me_5)_2Co$	PhCN	1 : 1 : 1	salt C_{60}^{n-} (n = 1, 2, 3)		50
$(C_5H_5)(C_6Me_6)Fe$			salt C_{60}^{n-} (n = 1, 2, 3)		151

[a] The compound gives a signal corresponding to $C_{60}^{-\bullet}$ in ESR spectra; [b] the compound gives an S-shaped magnetisation curve with hysteresis.[147]

Table 6. Salts of fullerenes with bulky cations.

Cation	Composition	Charge on the fullerene	Method of synthesis	Ref.
Ph_4P^+	$(Ph_4P)C_{60}(Ph_4PCl)$	–1	electrocrystallisation	57
	$(Ph_4P)C_{60}(Ph_4PCl)_2$	–1	"	56
	$(Ph_4P)_2C_{60}(Ph_4PBr)$	–1	"	152
	$(Ph_4P)_2C_{60}I_x$ ($0 < x < 1$)	–1	"	153
	$(Ph_4P)C_{70}(Ph_4PI)$	–1	"	154
Ph_4As^+	$(Ph_4As)C_{60}(Ph_4AsCl)$	–1	"	152
PPN^+ (**5**)	$(PPN)C_{60}(C_6H_5Cl)$	–1	"	48
	$(PPN)_2C_{60}$	–2	diffusion	50, 155
	$(PPN)_2C_{60}(PPNCl)MeCN$	–2	cationic metathesis	49
	$(PPN)_3C_{60}(MeCN)_2$	–3	the same	49
$Ru(biPy)_3^{2+}$	$[Ru(biPy)_3](C_{60})_2$	–1	electrocrystallisation	59

of the cations are drawn together to the six-membered rings of the fullerene in such a manner that the phenyl groups surround completely the $C_{60}^{-\bullet}$ radical anion. In the salt $C_{60}(PPN)_2$,[155] one fullerene molecule is surrounded by 22 phenyl groups of the cations, which efficiently shield the charge of the C_{60}^{2-} anion. According to X-ray diffraction data, there are no shortened distances between the fullerene anions in the crystal; the shortest distance between the centres of fullerene molecules is $\sim$12.5 Å.[152, 153, 155]

A study of the magnetic susceptibility of these salts[49] showed that they are paramagnetic.[49, 50] Apparently, the bulky cations surrounding the C_{60} fullerene radical anions interfere with their magnetic interaction. The magnetic susceptibility is determined by the spin ground state of fullerene radical anions. The magnetic moment of salts containing the $C_{60}^{-\bullet}$ and C_{60}^{3-} anions is 1.8 μ_B at room temperature, which corresponds to the singlet ground state with $S = 1/2$. At low temperatures, the magnetic susceptibility in $C_{60}^{-\bullet}$ salts decreases because of the weak antiferromagnetic interaction between the neighbouring fullerene molecules. The magnetic moment of $C_{60}^{2-\bullet}$ salts at room temperature was found to be 2.5 μ_B.[49, 50]

A study of the conductivity of these salts showed that all of them are semiconductors. The conductivity of the salt $[Ru(bipy)_3](C_{60})_2$ (Table 6) is 10^{-2} S cm^{-1}, and this salt is a semiconductor with an activation energy of 0.15 eV.[59] It has been shown[56,153] that the conductivity of the salts of $C_{60}^{-\bullet}$ with the Ph_4P^+ cation is from 10^{-7} to 10^{-4} S cm^{-1}. The low conductivity is apparently due to the large distances between the fullerene anions in these compounds.

9. Salts of the C_{60} fullerene with metalloporphyrins

The redox properties of metalloporphyrins also make it possible to use them for the reduction of fullerenes. For example, compound Cr(II)(TPP), where TPP is tetraphenylporphyrin, has strong donor properties ($E_{Ox} = -0.86$ V)[156] and reduces fullerene in tetrahydrofuran to $C_{60}^{-\bullet}$ to give the $[Cr(TPP)]C_{60}(THF)_3$ salt.[156] The reaction is reversible; the addition of toluene shifts the equilibrium towards the formation of neutral C_{60}. In pure toluene, the reduction of C_{60} does not occur. The $[Cr(TPP)]C_{60}(THF)_3$ salt is a paramagnetic with $S = 1/2$.[156]

The Sn(I)(TpTP) complex, where TpTP is tetra-*p*-tolylporphyrin ($E_{Ox} = -1.17$ V), in the presence of *N*-methylimidazole (*N*-MeIm) forms a salt with C_{60} with composition $[Sn(TpTP)](N\text{-MeIm})_2(C_{60})_2$. *N*-Methylimidazole stabilises the $Sn(TPP)^{2+}$ cation and hence facilitates the formation of the complex.[48]

10. Metal salts of fullerenes

a. Conducting properties of fullerene salts. Superconductivity

Reduction of fullerene results in the population of the t_{1u} energy levels, which can be populated with up to six electrons.[25, 36] Therefore, the compounds obtained can display conducting and superconducting properties if the degree of reduction x of the C_{60} fullerene ranges from 0 to 6.[13, 14, 25]

The character of conductivity in the salts $M_x \cdot C_{60}$ varies strongly depending on the degree of the fullerene reduction. At the degree of reduction $x = 1$, the salts $M \cdot C_{60}$ can display metallic conductivity.[61, 157–159]

The compounds M_3C_{60} have higher conductivity (*e.g.*, the conductivity of K_3C_{60} at room temperature was shown to be

2.5×10^{-3} S cm^{-1}) than the compounds M_xC_{60} with different stoichiometry. At low temperatures, the salts M_3C_{60} display metallic conductivity and can pass into the superconducting state.

The density of energy states at the Fermi level $N(E_F)$ (number of states eV^{-1}) is an important parameter determining the superconductivity transition temperature (T_c). Because of the small overlapping of the π-molecular orbitals of the neighbouring C_{60} molecules in the compounds M_3C_{60}, the conduction band is half occupied and has a width of 0.2–0.3 eV. At a small band width, the density of states at the Fermi level is rather high (25 states eV^{-1} for K_3C_{60} and 35 states eV^{-1} for Rb_3C_{60}, see Ref. 25). It is this fact that explains higher T_c values in fullerene salts with alkali metals in comparison with other known organic superconductors.[10]

In the compounds M_3C_{60} with face-centred cubic (FCC) lattice, an increase in the size of the alkali metal atom results in an increase in the distance (d) between the fullerene molecules in the crystal cell and a linear increase in T_c. The explanation for the latter phenomenon is that the increase in $d(C_{60}-C_{60})$ in M_3C_{60} decreases the overlapping of the π-molecular orbitals of the neighbouring fullerene molecules and, accordingly, the width of the conduction band. The narrowing of the conduction band increases the density of states at the Fermi level (as the number of states at the Fermi level does not depend on the band width and is constant) and increases the temperature of superconductivity transition (T_c).[13,14,28] However, if the distance between the centres of fullerene molecules in the crystal cell is more than 10.3 Å, the compound becomes a Mott dielectric.[161]

It was found that the M_2C_{60} and M_4C_{60} salts, in which the C_{60} molecule accepts two or four electrons, display only semiconductor properties with an activation energy of about 0.5 eV.[160] The significant difference of these phases from the M_3C_{60} phase may be due to a decrease in the symmetry of the fullerene molecule in these compounds. Partial removal of the degeneracy of the t_{1u} orbital and splitting of the conduction band into two bands (completely filled and vacant) with an energy difference between them of ~0.5 eV occurs in M_2C_{60} and M_4C_{60}.[160]

At $x = 6$, the conduction band is filled completely, and M_6C_{60} compounds are dielectrics.[13]

If more than six electrons are introduced in a C_{60} molecule, filling of the t_{1g} level starts; this level can accept six electrons. Therefore, metallic conductivity is displayed again and transition to the superconducting condition is possible at a degree of reduction of fullerenes, x, in C_{60} compounds from 6 to 12.[13,18]

The conductivity of C_{70} fullerene salts is little studied. Calculations show that M_xC_{70} phases, where M is an alkali metal and $x = 4$, can have metallic conductivity, while at $x = 1.8$ they can be semiconductors. For example, the K_4C_{70} phase actually has metallic conductivity but is not a superconductor down to 1.35 K.[13]

b. Intercalation of fullerenes

The crystals of the C_{60} fullerene have a densely packed FCC lattice[37] with relatively weak intermolecular bonds between separate molecules. This lattice contains two tetrahedral and one octahedral cavities per molecule with radii 1.10 Å and 2.06 Å, respectively, hence fullerene is a convenient object for intercalation. If the cavities are completely filled with the metal atoms, the composition of the compounds obtained has the formula M_3C_{60}. As the dopant size or the number of its atoms are increased (to $n = 6$), the densely packed FCC-lattice is transformed to a less dense volume-centred cubic (VCC) lattice with six equivalent tetrahedral cavities per C_{60} molecule.[13,14,28]

Diverse methods for the intercalation of fullerenes have been developed. In the most popular procedure for the synthesis of M_xC_{60} compounds, a fullerene and x equivalents of an alkali metal are placed in a quartz tube evacuated to 10^{-2}–10^{-5} Torr, which is then sealed and heated at 200–500 °C.[162] The intercalation of the C_{60} fullerene with alkali metal hydrides, borohydrides and azides and other reagents has also been described.[13,14]

The gas-phase intercalation of the C_{60} fullerene suffers certain drawbacks. In this case, it is difficult to control the degree of reduction of the fullerene; the formation of a mixture of M_xC_{60} phases with different content of the metal is possible (for example, M_3C_{60} contains the M_6C_{60} phase, which is a dielectric). An inevitable heterogeneity of the specimens formed complicates the study of the crystal and electronic structure of these materials.

Single crystals of these compounds are obtained by syntheses with $C_{60}^{-\bullet}$ and $C_{60}^{3-\bullet}$ radical anions in solutions.[153,154]

Refluxing a fullerene solution with a 90-fold excess of K or Rb in toluene results in a precipitate containing 1% of a superconducting K_3C_{60} phase and 7% of a superconducting Rb_3C_{60} phase.[163] The addition of 5%–30% of benzonitrile to toluene favours the electron transfer from the alkali metal to the fullerene and interferes with the precipitation of intermediate compounds with the $C_{60}^{-\bullet}$ and $C_{60}^{2-\bullet}$ anions, which allows one to obtain specimens with high content (up to ~50%) of the superconducting M_3C_{60} phase. Reduction of fullerene with an alkali metal in pure benzonitrile results in M_xC_{60} compounds, where $x = 4$, 5 and 6.[162] A drawback of the method is the presence of an unconsumed alkali metal among the reaction products.

Heating and stirring of a suspension of fullerene in *N*-methylimidazole with a high excess of a metal (Li, Na, Ba, Fe, Cu, Zn) resulted in the corresponding salts of $C_{60}^{-\bullet}$ and $C_{60}^{2-\bullet}$. The compounds have the formulas: $[M(N\text{-MeIm})_x]C_{60}$ and $[M(N\text{-MeIm})_x]_2C_{60}$, where $x = 4$–6.[148]

A series of compounds $M_xC_{60}(THF)_y$, where $x = 0.4$–3 and $y = 1$–14, have been obtained by the reaction of C_{60} with alkali metals in THF in the presence of 1-methylnaphthalene,[55] by cooling a C_{60} solution reduced with potassium in tetramethylethylenediamine[55] or by the reaction of C_{60} with $K[Mn(C_5Me_5)_2]$ in THF.[164] Salts with small x (~0.4) and y (~2.2) values have been obtained by electrochemical reduction of fullerene in the presence of an alkali metal tetraphenylborate.[61]

The anions $C_{60}^{3-\bullet}$ in the structure of $K_3C_{60}(THF)_{14}$ are packed in linear chains;[53] one of the K^+ ions is coordinated with a five-membered ring of C_{60} and serves as a bridge between two fullerene radical anions. The other two K^+ cations are located above and below the $C_{60}^{3-\bullet}$ anion, forming contacts with six-membered rings of C_{60}. The K^+ cations are also coordinated with THF molecules. Judging by the arrangement pattern of the $C_{60}^{3-\bullet}$ anions, the structure of $K_3C_{60}(THF)_{14}$ is similar to that of M_3C_{60} superconductors with an FCC lattice. However, the distance between the $C_{60}^{3-\bullet}$ ions is large, and this compound does not display metallic properties.[53] A compound with a different stoichiometry, *viz.*, $M_xC_{60}(THF)_y$, where $x \sim 0.4$ and $y \sim 2.2$, has a conductivity of 50 S cm^{-1} at room temperature, which increases with a decrease in temperature and is about 1000 S cm^{-1} at 100 K. This is probably due to incomplete charge transfer to the fullerene ($\delta = 0.4$) and the presence of small distances between C_{60} molecule centres along the crystallographic axis $\bar{c}$ (9.93 Å) in the crystal.[61]

After removal of tetrahydrofuran from the salt $K_3C_{60}(THF)_7$ by evacuation, keeping at constant temperature at 300 °C for 12 h and subsequent cooling to 103 °C, heat evolution in the sample is observed, which is explained by a transition to a more stable phase with an FCC lattice. As a result, the sample becomes a superconductor containing 31% of the superconducting K_3C_{60} phase.[164]

c. Fullerene polymerisation in MC_{60} and M_3C_{60} salts

The intercalation of C_{60} fullerene with alkali metals in stoichiometric ratio (1 : 1) gave the radical anionic salts KC_{60}, RbC_{60} and CsC_{60}.[157–159] On slow cooling of the intercalation products, [2+2]-cycloaddition of the neighbouring fullerene molecules occurs, which results in the polymerisation of $C_{60}^{-\bullet}$ into linear chains. The distance between the centres of fullerene molecules decreases to 9.11–9.13 Å.[157] Polymeric compounds are stable in air,[157] insoluble in tetrahydrofuran and depolymerise only on heating above 320 °C. A study of the conductivity of the resulting

polymeric specimens showed that $[KC_{60}]_n$ is a three-dimensional metal the conductivity of which slowly increases on decreasing the temperature to 4 K.[158] Magnetic measurements also show[159] that $[KC_{60}]_n$ behaves as a three-dimensional metal down to liquid-helium temperatures. Unlike $[KC_{60}]_n$, the $[RbC_{60}]_n$ and $[CsC_{60}]_n$ polymers are one-dimensional metals and pass to the dielectric state at 50 K and 40 K, respectively. At 25 K, the $[RbC_{60}]_n$ and $[CsC_{60}]_n$ polymers undergo magnetic transition with antiferromagnetic ordering of spins in the polymeric chain. The interaction between antiferromagnetic polymeric chains occurs through alkali metal atoms, which results in three-dimensional magnetic ordering of spins.[159]

The nature of conductivity in these compounds is not clear yet. It is possible that polymerisation of fullerenes results in π-conjugated bonds between the molecules and the conduction electrons can move through them along the fullerene chain. Another possible mechanism assumes that the carbon atoms that are not bound directly and correspond to the neighbouring fullerene skeletons approach each other with overlapping of the t_{1u} orbitals of these skeletons, and the conduction electrons move through these orbitals.[13] The second variant is more likely, as it has been shown[158] that the decrease in the ionic radius of the metal on going from rubidium to potassium results in overlapping of the t_{1u} orbitals of fullerenes belonging to different polymeric chains and to a change from one-dimensional to three-dimensional conductivity.

If C_{60} doped by alkali metals is rapidly cooled by liquid nitrogen, polymerisation cannot occur and monomeric radical anionic salts are obtained, such as KC_{60}, RbC_{60} and CsC_{60}.[157] Heating of monomeric KC_{60} above 77 K, or RbC_{60} and CsC_{60} above 160 K, results in dimerisation; the dimeric phase $K_2(C_{60})_2$ is a dielectric.[157]

It has been shown that the radical anion $C_{60}^{3-\bullet}$ in compounds M_3C_{60} can polymerise as well.[165] Na_2CsC_{60} polymerises with transition to an orthorhombic phase at a pressure of 3 kbar; the resulting polymer maintains superconducting properties.[165]

d. Superconducting compounds of C_{60}

To date, about thirty superconductors have been obtained based on C_{60}. Their superconducting transition temperatures range within 2–40 K (Fig. 3).

Compounds with composition M_3C_{60}, where M = K, Rb or a combination of K, Rb and Cs, with an FCC lattice (Fig. 3, *1*) have been studied in most detail.[12–14, 28] It was found for this series of compounds that T_c increases linearly with the size of the alkali metal atom and the distance between the centres of fullerene molecules, $d(C_{60}-C_{60})$, in the crystal cell.[13, 14, 28, 166] An increase in T_c is also observed in the reaction of the M_3C_{60} salts with ammonia. For example, the intercalation of Na_2CsC_{60} with ammonia results in $(NH_3)_4Na_2CsC_{60}$ with a similar crystal lattice, while the distance between the $C_{60}^{3-\bullet}$ radical anions increases from 9.99 Å to 10.23 Å. This is accompanied by an increase in T_c from 10.5 K in Na_2CsC_{60} to 29.6 K in $(NH_3)_4Na_2CsC_{60}$.[166] However, it was found[160] that the compound Cs_3C_{60} with the A15-type structure and distances between the fullerenes molecule ~10.35 Å is the Mott dielectric and becomes a superconductor with T_c = 40 K only at a pressure of 15 kbar.[160]

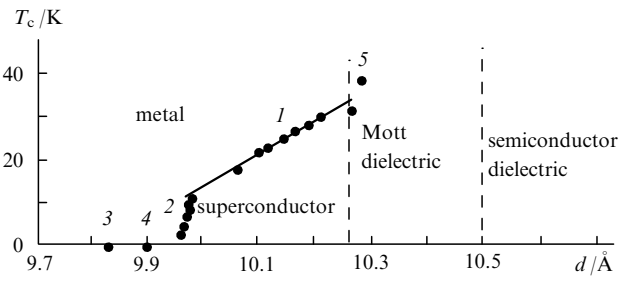


Figure 3. Phase diagram for the salts M_3C_{60}. Dependence of T_c on the closest distance (d) between the centres of C_{60} molecules in crystalline state at room temperature:[14] (*1*), experimental data for M_3C_{60} (K_3C_{60}, K_2RbC_{60}, K_2CsC_{60}, KRb_2C_{60}, Rb_3C_{60}, Rb_2CsC_{60} and $RbCs_2C_{60}$) with FCC lattice; (*2*), experimental data for the series $Na_2(Rb_xCs_{1-x})C_{60}$ with simple cubic lattice; (*3*), Li_2RbC_{60}; (*4*), Li_2CsC_{60}; (*5*), Cs_3C_{60} with A15 structure, which has superconductor properties under 15 kbar.

The salts M_xC_{60} have the highest temperature of superconductivity transition for $x = 3$.[28] If the stoichiometry deviates from this value in either direction, T_c starts to decrease, and at $x \leqslant 2$ and $x \geqslant 4$ the compounds no longer pass into the superconducting state.

On transition from one crystal lattice type to the other, the character of interaction between the neighbouring fullerene molecules changes. Therefore, the compounds Na_2MC_{60}, where M = K, Rb and Cs, with simple cubic lattice have a different dependence of T_c on the distance between the fullerene molecules than the compounds M_3C_{60} with FCC lattice. A minor increase in this distance in compounds with a simple cubic lattice strongly increases the T_c (Fig. 3, *2*).[14]

A weak covalent interaction Li–C in compounds Li_2MC_{60} (Fig. 3, *3*, *4*) changes their electronic structure, and these compounds do not display superconducting properties.[14]

A group of superconductors A_xC_{60} obtained by intercalation of C_{60} with alkaline-earth metals, *i.e.*, Ca, Sr and Ba, is of interest.[13, 18] Unlike M_3C_{60} (M = K, Rb, Cs), in which the population of the t_{1u} orbital occurs, the superconductivity in these compounds is due to the population of the t_{1g} orbital. The T_c of compounds A_xC_{60} ranges within 4–8.5 K and depends little on the distance between the fullerene ions.[13] The superconducting state is observed at different populations of the conduction band, but it is rather difficult to determine the exact extent of charge transfer (δ) to the fullerene. In the series of compounds Ca_xC_{60} with $x = 3-6$, Ca_5C_{60} has the maximum conductivity (the degree of charge transfer to C_{60} δ equals 10) and passes in the superconducting state at 8.4 K.[13, 18] The compounds Ca_3C_{60} ($\delta = 6$) and Ca_6C_{60} ($\delta = 12$) (the conduction band is completely populated) do not display metallic properties.[13, 18] As opposed to Ca_3C_{60} and Ca_6C_{60}, a weak covalent interaction of Ba and Sr with fullerene in Ba_3C_{60}, Ba_6C_{60}, Sr_3C_{60} and Sr_6C_{60} is possible because of the larger ionic radii of these metals. This results in a decrease in the actual charge transfer to the fullerene and in only partial population of the conduction band at $x = 3$ and $x = 6$.[18] Therefore, Ba_3C_{60} and Sr_3C_{60} display metallic properties, and Ba_4C_{60}, Sr_6C_{60} and Ba_6C_{60} have superconducting properties at T_c = 4, 7 and 4 K, respectively.[13, 18]

It has been shown[166] that C_{60} fullerene intercalated with lanthanides can also be a superconductor (for example, $Yb_{2.75}C_{60}$ has T_c = 6 K).

e. Intercalation of molecular complexes of C_{60} with alkali metals

Structural diversity of organic molecules allows one to create C_{60} compounds with different packing of the C_{60} molecules in the crystal, *viz.*, one-dimensional chains, two-dimensional layers or three-dimensional arrangement of the C_{60} molecules. Fullerene compounds with one-dimensional and two-dimensional packing of the C_{60} molecules are of special interest for the study of conducting and superconducting properties. In addition, by using different donor molecules, it is possible to control the distance between the fullerene molecules in the crystal lattice in order to obtain materials with high T_c. This stimulated studies of the intercalation of C_{60} complexes with alkali metals. The intercalation of molecular complexes of C_{60} is accompanied by reduction of the fullerene according to the scheme:

$$D^{\delta+}C_{60}^{\delta-}Sol \xrightarrow{Red} D(C_{60}^{n-}\, n\,Red^{+})Sol$$

Red is reducing agent.

The intercalation of C_{60} complexes with octamethylenetetrathiafulvalene (**10**) $(OM-TTF)C_{60}(C_6H_6)$ or bis(ethylenedioxy)-tetrathiafulvalene $[(BEDO-TTF)\sim C_{60}]$ with potassium and rubidium is carried out at $10^{-4}-10^{-5}$ Torr and 55 and 67 °C, respectively, as in the case of pure C_{60}.[168, 169] The intercalation of $(OM-TTF)C_{60}(C_6H_6)$ gave compounds with composition $K_x(OM-TTF)C_{60}(C_6H_6)$, where $x \leqslant 1.8$. Apparently, the solvent is retained in the compound.[168] Because of their small radii, the alkali metal atoms occupy the cavities in the structure of the starting molecular complex; this increases somewhat the parameters of its crystal cell.[169] The intercalation of $(OM-TTF)C_{60}(C_6H_6)$ with potassium gives a superconducting phase with a transition temperature of 17–18.8 K, and that with rubidium gives a superconducting phase with $T_c = 23-26$ K. The intercalation of $[(BEDO-TTF)\sim C_{60}]$ with potassium yields a superconducting phase with $T_c = 15$ K.[168, 169]

f. Intercalation of fullerenes and their complexes with halogens

The intercalation of fullerenes with molecular iodine (I_2) and interhalides, *viz*., IBr and ICl, gives the complexes $(Hal_2)_xC_{60}$. The reaction is carried out at 100–250 °C in evacuated tubes.[40, 170, 171] The content (x) of the halogen in the sample can vary from 0.2 to 2,[170–172] depending on the conditions and duration of intercalation. A study of the structure of the $(I_2)_2C_{60}$ complex has shown that it has a layered structure; the C—I distances (3.6–4.0 Å) are smaller than the sum of the van der Waals radii of carbon and iodine.[170] There is no charge transfer from the fullerene to iodine in these compounds. Iodine is weakly bound to the fullerene and is removed from the compound at 200 °C.[170] $(I_2)_2C_{60}$ is a dielectric the conductivity of which is less than 10^{-9} S cm^{-1} (Ref. 170).

A study of the magnetic properties of C_{60} complexes obtained by intercalation of fullerene with I_2, ICl and IBr revealed magnetic transitions[40, 171] at 60 K, 30 K and 30 K, respectively. For pure C_{60} and C_{70} fullerenes, these are also are observed at 60 K.[38] Apparently, these magnetic transitions, like those in the case of pure fullerenes, are due to transition of the specimens to the frozen glassy magnetic state,[38] because synchronisation of rotation of the C_{60} molecules is also possible in the presence of shortened contacts between the C_{60} molecules in the crystals of these molecular complexes at low temperatures. Cooling of these specimens in a magnetic field below this temperature results in freezing of a completely ordered orientation of the magnetic moments of the fullerene molecules.

The intercalation of the complexes $(DB-TTF)C_{60}(C_6H_6)$, $(TMDTDM-TTF)_2C_{60}(CS_2)_3$ and $TPDP(C_{60})_2(CS_2)_4$ with iodine results in compounds with a high content of iodine, *viz*., $(DB-TTF)C_{60}I_9$, $(TMDTDM-TTF)_2C_{60}I_{7.5}$ and TPDP.$(C_{60})_2I_{10}$.[173, 174]

The intercalation of C_{60} complexes with iodine is based on the solid-phase oxidation of the donor component of these complexes with the formation of a radical cation. The solvent, for example, CS_2, is displaced by iodine.[174]

$$D^{\delta+}C_{60}^{\delta-}Sol \xrightarrow{Ox} (D^{n+}\, n\,Ox^{-})C_{60}$$

Ox is oxidant.

The intercalation is accompanied by noticeable changes in the ESR spectra due to the oxidation of the donor.[173] The optical absorption spectra display a shift (up to 10 nm) of the absorption bands of the basic electron transition ε_0 at $\lambda = 260$ and 350 nm and an increase in absorption intensity in the region of 450–620 nm.[173] These changes can be due to the formation of a radical cation by the donor.[173] The position of the absorption band of the $T_{1u}(4)$ vibrations of C_{60} (1429 cm^{-1}) in the IR spectrum of intercalated specimens is not changed, which indicates the absence of charge transfer to the fullerene molecule. The starting complexes are dielectrics. Intercalation results in an insignificant increase in the conductivity of the complexes (by a factor of less than 100), which is apparently due to the large distances between the donor molecules in these complexes.[174]

IV. Structure and spectral characteristics of complexes and radical ionic salts of fullerenes

1. Specific features of the crystal structure

The position of the C_{60} molecules in a crystal and the number of direct van der Waals contacts between the fullerene molecules make it possible to distinguish several structural types of fullerene compounds.[175]

1. Three-dimensional packing of the C_{60} fullerene molecules with distances between the centres of the molecules ranging from 9.8 to 10.3 Å is observed in fullerene salts M_xC_{60} ($x = 1-6$) with alkali and alkaline-earth metals. Simple cubic, cubic face-centred, cubic volume-centred and rhombic lattices with the number of closest neighbouring C_{60} molecules from 8 to 12 correspond to this type of packing.[13, 14]

2. Layered packing, in which two-dimensional dense or loose hexagonal layers of C_{60} molecules are formed. The number of closest neighbouring fullerene molecules ranges from 4 to 6. The layers of donor molecules in these structures also alternate with layers of C_{60} molecules. In the donor layer, *e.g*., in the $(TMDTDM-TTF)_2C_{60}(CS_2)_3$ complex,[103] there are also shortened contacts between the TMDTDM–TTF molecules. A shift of hexagonal layers relative to each other with transition to simple hexagonal packing of layers can be observed in compounds with small donors. This refers to compounds of C_{60} with such molecules as I_2,[170] S_4N_4,[95] P_4,[93] TMPD,[129] OM–TTF,[5] TPDP[109] or DAN.[44]

The structure of the $(DAN)C_{60}(C_6H_6)_3$ complex with layered packing of C_{60} molecules is shown in Fig. 4. Each C_{60} molecule in this complex is surrounded by four fullerene molecules with a distance of 10.07 Å between the centres.

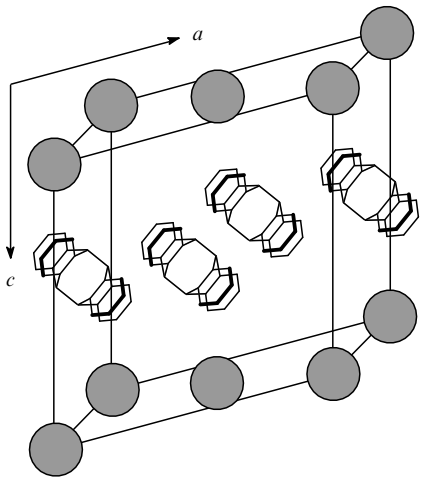


Figure 4. Projection of the crystal structure of the complex $(DAN)C_{60}(C_6H_6)_3$ (the positions of the fullerene molecules are indicated with grey spheres) along the crystallographic axis $\bar{b}$ [44] (schematic representation). The solvate benzene molecules (not shown) are located in the dianthracene layer.[44]

3. Cage packing: the fullerene molecules form various cavities or channels, in particular, hexagonal channels, which are filled with donor molecules. The number of the closest neighbouring fullerene molecules can vary from 4 to 8. This structure is represented by compounds of C_{60} with *twin*-TDAS,[113] C_6H_6[68, 69] and S_8.[90, 91]

4. Chain packing: the fullerene molecules form densely packed chains (with two closest neighbouring fullerene molecules) or double chains (with three closest neighbouring fullerene

molecules). This structure is characteristic of complexes of fullerene with BEDT–TTF,[98,99] *twin*-BEDT–TTF[102] and C_1TET–TTF.[110]

5. Island mode of packing: in this case, there are no direct van der Waals contacts between the fullerene molecules, and all distances between the centres of C_{60} molecules are ~12 Å. This type of packing is observed in compounds with large donor molecules (HMT,[115] Ph_3Sb[116]) or cations (Ph_4P^+ (see Refs 57, 136 and 153) and PPN^+ (see Refs 58 and 155).

The structures of some fullerene complexes, for example with such donors as DBTTF[105] and BTX, are intermediate between the cage and island structures.[111] Figure 5 presents the structure of the DBTTF·C_{60}·C_6H_6 complex. It is characterised by isolated packing of C_{60} molecules, in which each of them is surrounded by six closest neighbouring fullerene molecules with a distance of 10.4–10.5 Å between the centres. This distance is larger than the van der Waals diameter of fullerene (10.18 Å) but smaller than the distance characteristic of island structures (~12 Å).

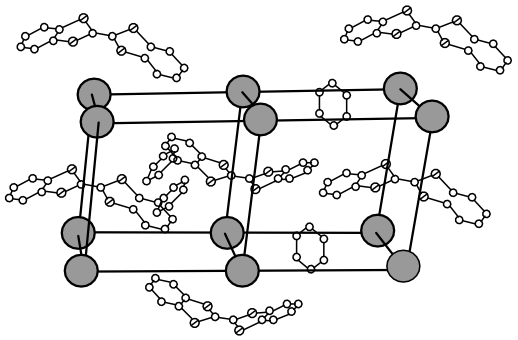


Figure 5. Crystal packing of the complex (DB–TTF)C_{60}·C_6H_6 (positions of fullerene molecules are indicated by grey spheres; crystallographic axes are shown by straight lines).[100]

Table 7 lists the mean bond lengths of the C_{60} fullerene molecule in its compounds. It is evident that the bond lengths in C_{60} change with an increase in the degree of charge transfer to the fullerene molecule; in this case, the 6–5 bonds shorten while the 6–6 bonds elongate. The direction of changes in the bond lengths upon reduction of fullerene is due to the nature of the t_{1u} orbital, which is anti-bonding with respect to the 6–6 bonds and bonding with respect to the 6–5 bonds.[13] This results in elongation of the fullerene molecule, and the C_{60} sphere is distorted to become an ellipsoid.

Table 7. Lengths of 6–5 and 6–6 bonds for D–A complexes and radical ionic salts of C_{60}.

Compound	Charge on C_{60}	6–5 Bond length/Å	6–6 Bond length/Å	Ref.
C_{60}	0	1.467(2)	1.355(9)	176
$C_{60}(SbPh_3)_6$	0	1.452(5)	1.383(4)	116
C_{60}(BEDT–TTF)$_2$	0	1.452(1)	1.389(7)	98
$C_{60}[(C_5H_5)_2Fe]_2$	0	1.450(5)	1.387(6)	145
$(C_{60})_2TPDP(CS_2)_4$	0	1.451(6)	1.381(6)	109
$C_{60}(S_8)_2$	0	1.448(8)	1.340(8)	90
$C_{60}[Ni(C_5Me_5)_2]CS_2$	−1	1.449(3)	1.389(3)	149
$C_{60}[Co(C_6H_5)_2]CS_2$	−1	1.453(4)	1.384(8)	47
$C_{60}(PPN)_2$	−2	1.446(2)	1.399(2)	155
K_3C_{60}	−3	1.452(1)	1.400(4)	13
K_6C_{60}	−6	1.432(1)	1.445(3)	13

2. Stability

The stability of fullerenes with respect to atmospheric oxygen differs from the stability of their compounds. In solid state, fullerenes can adsorb oxygen on their surface.[62] In solution, they can add oxygen under illumination to give epoxides $C_{60}O_n$, where $n = 1, 2$ and 3 (therefore, it is preferable to carry out reactions with fullerenes in the dark).[19] Anionic fullerene compounds are particularly sensitive to oxygen because of the possible reaction

$$C_{60}^{n-} + n\,O_2 \longrightarrow C_{60} + n\,O_2^-.$$

This reaction can also yield addition products $C_{60}O_2^{-\bullet}$ at the fullerene 6–6 or 6–5 bonds.[177]

In aprotic media, the redox potential of the $O_2/O_2^{-\bullet}$ couple is −0.8 V,[48] while the first redox potential of fullerenes, $C_{60}/C_{60}^{-\bullet}$ and $C_{70}/C_{70}^{-\bullet}$, is −0.4 V.[31] With these values of redox potentials, oxidation of fullerene radical anions $C_{60}^{-\bullet}$ and $C_{70}^{-\bullet}$ is thermodynamically unfavourable, and hence radical monoanionic fullerene compounds should be stable when exposed to air. This is actually observed for salts containing the $C_{60}^{-\bullet}$ radical anion (KC_{60}, RbC_{60}, CsC_{60}) and salts with bulky cations.[56–58,152–154,157] The instability of salts of $C_{60}^{-\bullet}$ with metalloporphyrins,[48] metallocenes[48,147] and amines[15,134] in the air can be due to the fact that protons or metal cations can stabilise the charge on $O_2^{-\bullet}$. The redox potential of the $O_2/O_2^{-\bullet}$ couple becomes more positive due to stabilisation of the $O_2^{-\bullet}$ radical anion, which enables the oxidation of $C_{60}^{-\bullet}$.

The second redox potential of fullerenes $C_{60}^{-\bullet}/C_{60}^{2-}$ and $C_{70}^{-\bullet}/C_{70}^{2-}$ is ~−0.8 V,[31] hence the oxidation of fullerene dianions with oxygen is thermodynamically favourable. Therefore, radical anionic salts containing fullerene dianions or C_{60}^{n-} anions in higher degrees of reduction are very sensitive with respect to oxygen.[82]

3. Thermogravimetry

Derivatography is generally used to study the thermal stability of both pure fullerene and its compounds.[43,44,54,75,101,104,178] Heating in air causes complete combustion of fullerene at 650 °C. In nitrogen, fullerene starts to sublime at 600 °C, and the maximum sublimation rate is reached at 700–800 °C.[178]

It is possible to determine the content and the strength of binding of a solvent in a complex from derivatograms of molecular complexes of fullerenes.[43,44,54,75,101,104] Thermogravimetric studies of fullerene complexes show that partial decomposition of donors occurs in these compounds. The decomposition temperatures of donors in complexes are close to those of the pure donors. In certain instances, the decomposition temperature of a donor increases owing to its stabilisation because of the donor-acceptor interaction with the fullerene.[44,54,75] The presence of a large amount of a solvent in a molecular complex separates the fullerene molecules from each other. Therefore, the sublimation temperature of the fullerene in such complexes even after complete removal of the solvent is lower[43,50,103] than that of pure C_{60}.[178]

4. Spectroscopy of compounds based on fullerenes

A significant number of publications deal with the study of fullerenes and their compounds by spectroscopic methods (see, for example, Refs 5, 22–26, 36 and 179–195).

a. Electronic spectroscopy

Optical spectroscopy is a convenient method for the study of changes in the electronic structure of fullerenes upon formation of donor–acceptor compounds.[5,9,181–185]

The optical absorption spectrum of the C_{60} fullerene in solid state (Fig. 6) has been studied in detail.[25,66] In the ultra-violet region (250–400 nm), two intense bands corresponding to symmetry-allowed electronic transitions are observed. There is a rather strong band in the visible region (λ = 420–540 nm) with a maximum at λ = 450 nm (2.7 eV), the origin of which is not quite clear. This band is absent in the absorption spectra of C_{60} solutions,[25] but appears, for example, upon aggregation of several

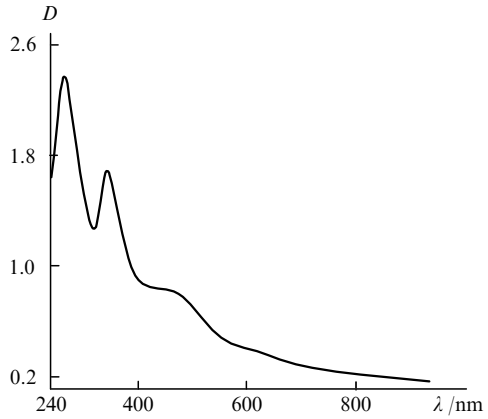


Figure 6. The absorption spectrum of C_{60} in a KBr matrix.[181]

C_{60} molecules in a complex with γ-cyclodextrin in aqueous solution.[84] Therefore, this band is sometimes[179] related to intermolecular transfer of an electron from the HOMO of the C_{60} molecule to the LUMO of the neighbouring C_{60} molecule. The absorption at $\lambda = 540-620$ nm (2.2–2.0 eV) has low intensity and corresponds to the symmetry-forbidden $h_u \rightarrow t_{1u}$ transition from HOMO to LUMO of one C_{60} molecule (see Fig. 1).[25] The manifestation of this forbidden transition both in liquid and in solid phase is explained by a deviation of the symmetry of C_{60} molecules from I_h.[25] The absorption edge of fullerene in optical spectra is in the region of 1.95–1.75 eV, which corresponds to 640–700 nm, and it is basically related to exciton transitions.[180]

The formation of molecular complexes does not induce considerable changes in the electronic system of fullerenes.[181] Irrespective of the solvent, the absorption edge of fullerene in fullerene solvates shifts by 0.1 eV upfield in comparison with pure fullerene,[180] which is explained[185] by separation of fullerene molecules from each other by the solvent.

The spectra of complexes both in solution and in solid state display charge-transfer bands (CTB) from the donor to the fullerene. The process of charge transfer for complexes with an uncharged ground state upon absorption of a light quantum is described by the scheme:

$$D^{\delta+}A^{\delta-} \xrightarrow{h\nu} D^{(1+\delta)+}A^{(1+\delta)-}.$$

The dependence of the charge transfer energy ($h\nu_{CT}$) on the donor IP for complexes of one acceptor with a series of donors is linear. This dependence is described by the equation:[5,9]

$$h\nu_{CT} = \alpha(IP - EA) - E_C,$$

where α is a constant, IP is the ionisation potential of the donor, EA is the electron affinity of the acceptor, and E_C is the energy of electrostatic interaction between the donor and acceptor radical ions in the excited state of the complex.

Such a dependence for complexes of the C_{60} fullerene with substituted anilines[182] and naphthalenes[183] (IP = 7.2–8.13 eV) in toluene is shown in Fig. 7 and can be described by the expression: $h\nu_{CT} = 0.91IP - 4.34$ (eV).

Table 8 lists the energies corresponding to the maximum of the charge-transfer band for a number of C_{60} complexes in the solid state. It is evident that $h\nu_{CT}$ decreases with a decrease in the redox potential ($E_{Red/Ox}$) of the donors.[5]

Irradiation of a crystalline complex (TMPD)C_{60} with visible light (He–Ne laser) was found to cause a strong increase in the absorption at 1070 nm.[76] This is related to the formation of a long-lived radical anion $C_{60}^{-\bullet}$ upon transfer of an electron from TMPD to C_{60}. The lifetime of the $C_{60}^{-\bullet}$ radical anion in a crystal is about 1 h, which is several orders larger than the lifetime in the case of similar electron transfer in solution.[76]

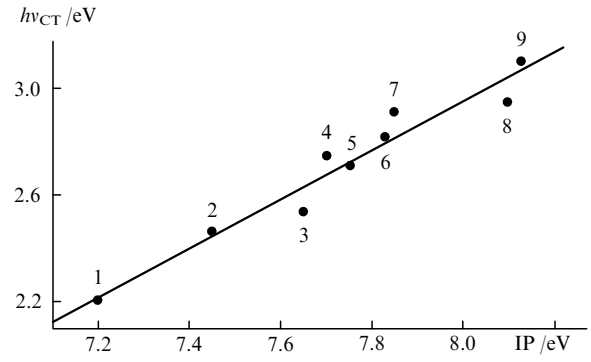


Figure 7. Dependence of charge transfer energy $h\nu_{CT}$ on ionisation potentials of donors in CTC of C_{60} in toluene: (*1*), *N*,*N*-diethylaniline;[182] (*2*), *N*,*N*-dimethylaniline;[182] (*3*), *N*-methylaniline;[182] (*4*), 1-methoxynaphthalene;[183] (*5*), 2,6-dimethylaniline;[182] (*6*), *o*-toluidine;[182] (*7*), 1-methylnaphthalene;[183] (*8*), aniline;[182] (*9*), 1-chloronaphthalene.[183]

Table 8. Position of the charge-transfer band maximum in electronic absorption spectra of C_{60} complexes in solid state.

CTC	$h\nu_{CT}$ /eV	$E_{Red/Ox}$ of the donor /V	Ref.
$[(C_5Me_5)_2Fe]_2C_{60}$	1.13	−0.086	147
(OM–TTF)$C_{60}(C_6H_6)$	1.35	+0.29	5
(TMDTDM–TTF)$_2C_{60}(CS_2)_3$	1.38	+0.39	104
(BEDO–TTF) ~ C_{60} [a]	1.51	+0.42	5
(BET–TTF)$C_{60}(C_6H_5Me)$	1.55	–	101
(BEDT–TTF)$_2C_{60}$	1.65	+0.52	98
(*twin*-BEDT–TTF)$C_{60}(CS_2)$	1.65	–	110

[a] The exact complex composition has not been determined.

Charge transfer from the donor to the fullerene in the ground state is related to the population of the t_{1u} orbital of the C_{60} fullerene. This enables electronic transitions from the t_{1u} orbital to vacant molecular orbitals with higher energies (see Fig. 1), which results in the appearance of new absorption bands in the near IR region. Their position corresponds to definite charge of the fullerene molecule:

Fullerene	$C_{60}^{-\bullet}$	C_{60}^{2-}	$C_{60}^{3-\bullet}$	C_{60}^{4-}	$C_{70}^{-\bullet}$	C_{70}^{2-}
ν (nm)	1070	950	780	730	1370	1165
			1380	1195		
Ref.	35, 48, 184	50	35	88	35	35

b. IR spectroscopy

The change in the symmetry and redistribution of the electron density upon formation of D–A complexes and radical ionic salts of fullerenes is reflected in their IR spectra.[9,25,26,184–195]

Due to its high symmetry (I_h), the C_{60} molecule has 46 characteristic normal vibrations. Four of these are active in the IR spectra [$T_{1u}(1-4)$ vibrations with absorption bands at 527, 577, 1183 and 1429 cm^{-1}, respectively] and ten in Raman spectra; 32 normal vibrations in the C_{60} molecule are symmetry-forbidden in the dipole approximation.[25,26,186]

In the crystalline C_{60} fullerene[186] and some of its crystal solvates,[187,188] violation of symmetry of the environment of the C_{60} fullerene molecules is observed, which results in partial modification of symmetry-forbidden vibrations, hence they appear in the IR spectra. This is due to the presence of defects, dislocations, admixtures or solvent molecules in the crystal structure of C_{60} and in crystal solvates.

At room temperature, the molecules of the C_{60} fullerene in crystals rotate quickly and isotropically, occupying positions with the T_h symmetry.[188] The T_{1u} vibrations, which are active in IR

spectra of the C_{60} fullerene, are threefold degenerate and appear as single bands. Cooling C_{60} crystals below 255 K results in an orientational-type phase transfer with freezing of the rotation of the fullerene molecules and a decrease in its position symmetry to S_6.[189] The degeneration of the $T_{1u}(4)$ vibration of C_{60} at 1429 cm^{-1} is eliminated, and at 8 K it is split into three bands with wave numbers 1424.5, 1427.9 and 1431.2 cm^{-1}. The $T_{1u}(3)$ vibration at 1183 cm^{-1} remains unsplit.[189] Similar splitting of the $T_{1u}(4)$ vibration of C_{60} into three bands (Table 9) has been reported in compounds of C_{60} with amines, *viz*., $(TMPD)C_{60}$ and $(TPA)C_{60}$.[190] This splitting is due to freezing of rotation of the C_{60} molecules in the crystal of the complex due to the intermolecular interaction with molecules of the donor and a decrease in the positional symmetry of the C_{60} molecules (in comparison with pure fullerene above 255 K).[190]

Table 9. Position of the $T_{1u}(4)$ vibration band of fullerene (ν) and degree of charge transfer (δ) estimated from Eqn (2) in donor–acceptor complexes and radical ionic salts of C_{60}.

Compound	ν /cm^{-1}	Compound type	δ	Ref.
C_{60}	1424, 1428, 1431,[a, b] 1429 [c]			189
$S_4N_4C_{60}$	1429	molecular complex	0	75
$(S_8)_2C_{60}(C_6H_5Cl)_{0.5}$	1429	the same	0	194
$(TPA)C_{60}$	1425, 1428, 1433 [b]	"	–	190
$(TMPD)C_{60}$	1422, 1425, 1427 [b]	CTC	–	190
$(C_5H_5)_2CoC_{60}(CS_2)$	1411	CTC	~0.5	47
$(C_5H_5)_2CoC_{60}(C_6H_5CN)$	1413	CTC	~0.5	48
$(C_6H_6)_2CrC_{60}$	1407	CTC	~0.7	150
$[Na(18\text{-}C\text{-}6)]C_{60}(THF)_3$	1395	salt	~1	48
$(Ph_4P)C_{60}(Ph_4PCl)$	1394	"	~1	184
$(Ph_4P)C_{60}(Ph_4PI)$	1394	"	~1	195
RbC_{60} [d]	1392	"	~1	26, 191
$(Ph_4As)C_{60}(Ph_4AsCl)$	1390	"	~1	184

[a] Measured at 8 K; [b] splitting of the $T_{1u}(4)$ band of fullerene on freezing the rotation in the crystal; [c] measured at 293 K; [d] film.

The transfer of electron density from the donor to the C_{60} fullerene in the ground state results in a shift of some of its bands in the IR and Raman spectra.[26, 191, 192] This is caused by the population of the t_{1u} orbital of the fullerene and interaction of the T_{1u} vibrations with virtual electronic transitions from the t_{1u} orbital to the higher t_{1g} orbital.[191] Figure 8 shows the charge dependence of the position of absorption bands (ν) of C_{60} vibrations active in the IR spectrum.[26, 191] The $T_{1u}(4)$ and $T_{1u}(2)$ vibrations are most sensitive to charge transfer: they are characterised by a linear increase in ν_p and an almost linear shift of ν. The $A_{1g}(2)$ vibration active at 1469 cm^{-1} in the Raman spectrum also has a linear dependence of ν on the degree of reduction of the fullerene molecule.[26, 192] This relationship may be used for the determination of the degree of C_{60} reduction in salts,[26] including that occurring during intercalation. The plasma frequency (ω_p) (square root of the oscillator force) also changes linearly with the charge on the fullerene molecule (Fig. 9).

The change in frequency of absorption bands in the IR spectrum of C_{60} vibrations in D–A complexes makes it possible to estimate even a small degree of charge transfer ($0 < \delta < 1$). This method has already been used previously for the estimation of charge transfer in organic CTC.[9, 193]

The $T_{1u}(4)$ vibration is most suitable for determination of the degree of charge transfer (δ), as the transition from C_{60} to the $C_{60}^{-\bullet}$ radical anionic salts is accompanied by a strong shift of the absorption band of this vibration from 1429 cm^{-1} to 1390–1395 cm^{-1} (see Refs 26, 48, 184, 191 and 195) (Table 9).

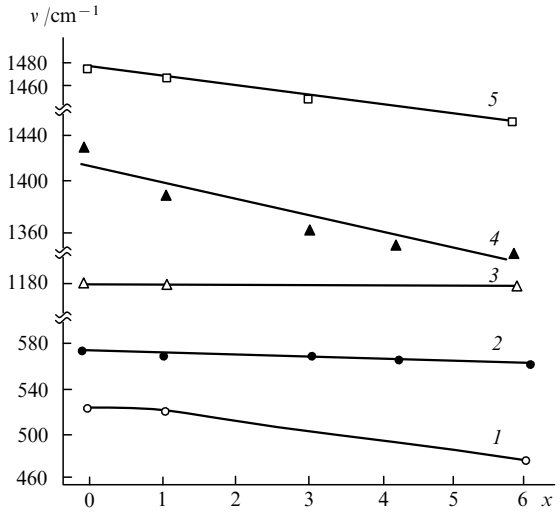


Figure 8. Wave numbers (ν) for different degrees of reduction (x) of the C_{60} fullerene molecule.[191] (*1*), $T_{1u}(1)$ vibrations; (*2*), $T_{1u}(2)$ vibrations; (*3*), $T_{1u}(3)$ vibrations; (*4*), $T_{1u}(4)$ vibrations; (*5*), $A_{1g}(2)$ vibrations.

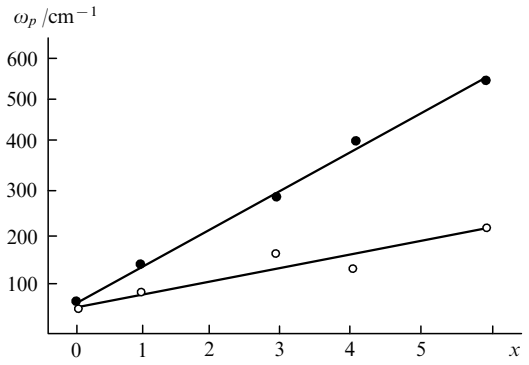


Figure 9. Plasma frequency (ω_p) for different degrees of reduction (x) of the C_{60} fullerene molecule.[191] (*1*), $T_{1u}(2)$ vibrations; (*2*), $T_{1u}(4)$ vibrations.

The change in the positions of absorption bands of three other T_{1u} vibrations active in the IR region on transition from C_{60} to $C_{60}^{-\bullet}$ is less marked.[26, 192]

Taking into account the linear dependence of the position of the absorption band of the $T_{1u}(4)$ vibrations on the degree of reduction of the fullerene molecule, it is possible to use Eqn (1) for the estimation of the degree of charge transfer in complexes:[9, 193]

$$\delta = \frac{2\Delta\nu}{\nu_0(1 - \nu_1^2/\nu_0^2)}, \qquad (1)$$

where ν_0 is the position of the absorption band of the $T_{1u}(4)$ vibration in neutral C_{60} (1429 cm^{-1}); ν_1 is its average position in $C_{60}^{-\bullet}$ salts [1392.5 ± 2.5 cm^{-1}, depending on the crystal structure (Table 9)], and $\Delta\nu$ is the difference between the positions of absorption bands of $T_{1u}(4)$ vibrations in neutral C_{60} and in the corresponding complex.

The use of these values in Eqn (1) gives Eqn (2):

$$\delta \cong 0.03\,\Delta\nu. \qquad (2)$$

The accuracy of estimation of charge transfer δ, which is ±0.03, depends on the accuracy of measurement of the positions of absorption bands in IR spectra (±1 cm^{-1}).

One can see from Table 9, which lists the positions of the $T_{1u}(4)$ vibration bands and the degree of charge transfer in C_{60} compounds estimated from Eqn (2), that the degree of charge transfer is close to zero (molecular complexes) for the majority of C_{60} compounds with organic donors. In radical ionic salts, the

degree of charge transfer is close to unity. Only the complexes of C_{60} with TMPD,[190] cobaltocene[47,48] and dibenzenechromium[150] have intermediate degrees of charge transfer.

c. ESR spectra

The *g*-factors and ΔH of ESR signals of fullerenes and their compounds are listed in Table 10. In a discussion of the ESR spectra of C_{60} compounds, it is necessary to emphasise the presence of two ESR signals at room temperature in specimens of the initial, 'pure' fullerene, one with $g = 2.0025-2.0021$ and $\Delta H = 2$ G[196,197] and the other with $g = 2.0006-2.0012$ and $\Delta H = 0.5-2$ G;[196] their widths virtually do not change down to liquid-helium temperatures. These signals originate from defects, *i.e.*, paramagnetic admixtures formed upon oxidation of fullerene with oxygen.[177,196] The intensity of the former signal increases by an order of magnitude on heating the specimen in air at 623 K for 2 h and by two orders on heating for 24 h.[196] The intensity of this signal changes considerably depending on the way the fullerene has been obtained or stored.

Unlike the signals related to the oxidation of fullerenes, the ESR signals of the C_{60}^{n-} anions have a considerably larger line width ($\Delta H = 20-60$ G), which depends strongly on temperature. The ground state of the radical anion $C_{60}^{-\bullet}$ is a singlet ($S = 1/2$) with $g = 1.997-1.999$. This value is smaller than the *g*-factor of a free electron.[56,56,61,153] Larger *g*-factors (2.0008) are observed only in salts of C_{60} with amines.[38,142] The C_{60}^{2-} anion displays a signal with $g = 2.0010$ and $\Delta H = 10-30$ G at room temperature. This corresponds to the triplet state ($S = 1$) with forbidden splitting $D \cong 0$: two electrons with parallel spins are so distant from each other that they behave similarly to electrons with independent spins, therefore their interaction is not displayed in the ESR spectra.[50] The radical anion $C_{60}^{3-\bullet}$ is in a singlet basic state ($S = 1/2$) at room temperature, and its *g*-factor equals $2.0012-2.0017$, and $\Delta H = 10-30$ G.[49] In the compounds M_3C_{60}, the ESR parameters (the *g*-factor and ΔH) of the $C_{60}^{3-\bullet}$ radical anion depend on the nature of the metal.[13,14] The ESR signals of all of the C_{60}^{n-} anions become much narrower as the temperature is decreased.[58,153,154]

Due to the Jahn–Teller effect, the presence of fullerene radical anions in C_{60} salts with bulky counter-ions results in violation of the I_h symmetry of C_{60}.[48–50,149] The effect can be both dynamic and static on the ESR time scale.[198] At room temperature, a dynamic effect with fast transition from one static Jahn–Teller configuration to the other is observed. Based on the ESR data, the frequency of this pseudo-rotation is estimated as $\sim 10^{12}$ Hz.[198] If the temperature is decreased, pseudo-rotation is hindered, the ESR signal narrows, and transition to the static Jahn–Teller effect is observed. In the salt $(Ph_4P)C_{60}(Ph_4PCl)_2$, this transition occurs when the temperature is decreased to 70 K;[199] this is accompanied by abrupt narrowing of the signal. On further decreasing the temperature, its width almost does not change. The static Jahn–Teller effect at low temperatures (4–70 K) results in transformation of the isotropic ESR signal to anisotropic. For instance, the $Na(18\text{-crown-}6)C_{60}(THF)_3$ salt displays an anisotropy of the *g*-factor: $g_\perp = 1.9968$, $g_\parallel = 2.0023$.[48]

As the symmetry of the $C_{60}^{-\bullet}$ radical anion decreases from I_h to D_{5d}, the T_{1u} state splits into two states, *viz.*, E_{1u} and A_{2u} (Fig. 10). The difference between the energies of the E_{1u} and A_{2u} states is small and equals 1 kcal, therefore thermal population of the overlaying A_{2u} state can occur, and an additional 'high-temperature' signal with $g = 2.000$ appears in the ESR spectrum of $C_{60}^{-\bullet}$.[48]

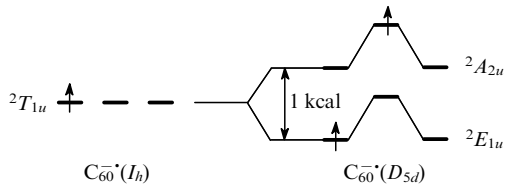


Figure 10. Scheme of partial removal of degeneration of the t_{1u} orbital in the $C_{60}^{-\bullet}$ radical anion upon lowering the symmetry from I_h to D_{5d}.[48]

The radical anion $C_{70}^{-\bullet}$ in the $(Ph_4P)_2C_{70}I$ salt gives a broad ESR signal with $g = 2.047$,[154] as does that in the salt $(TDAE)C_{70}$, with $g = 2.0022$.[136,137] Higher fullerenes display a narrow signal with $g = 2.0023$,[143] which is close to the *g*-factor for the free electron.

The ESR signal of the $C_{60}^{-\bullet}$ radical anion in some fullerene complexes has been used to determine the degree of charge

Table 10. *g*-Factors and line widths (ΔH) for ESR signals in D-A complexes and radical ionic fullerene salts.

Compound	Charge on fullerene	*g*-Factor	T/K	ΔH/G	Ref.
C_{60}	0	2.0021	< 300 [a]	0.3–1.0	196
C_{60}	0	2.0023	< 300 [a]	0.5–2.0	197
		2.0006–2.0012	< 300 [a]	0.5–2.0	
$(Ph_4P)C_{60}(Ph_4PCl)_2$	−1	1.9991	300	45	56
$(PPN)C_{60}(C_6H_5Cl)$	−1	1.9992	300(77) [b]	35(5)	58
		2.0007	> 50 [c]	1–2	
$(Ph_4P)_2C_{60}I_{0.35}$		1.9979	300(113) [b]	50(14)	153
$KC_{60}(THF)_5$	−1	1.9987	300	34	55
$Na_{0.4}C_{60}(THF)_{2.2}$	−0.4	1.999	300	30	61
$(TDAE)C_{60}$	−1	2.0008	300	22	38, 142
		2.0017–2.0030	< 16 [a,d]	30	
$(TDAE)C_{70}$	−1	2.0022	< 300 [a]	10	136, 137
$(TDAE)C_{84}$, C_{90}, C_{96}	−1	2.0020–2.0022	< 300 [a]	1.85–2.40	143
(DBU, DBN)C_{60}	−1	–	300(5) [b]	40(5)	127, 128
$[(C_5H_5)_2Co]C_{60}(C_6H_5CN)$	−1	1.9969	130(4.5) [b]	24(6)	48
		2.000	> 24 [c]	3	
$(Ph_4P)C_{70}(Ph_4PI)$	−1	2.047	300(4.2) [b]	600(1.5)	154
$SbCl_3 + C_{60}$	+1	2.0029	300	1.5	35
$(CB_{11}H_6Br_6)C_{76}$	+1	2.0030	300	0.5	7

[a] The signal is observed below the temperature T; [b] the ESR signal was measured at two different temperatures $T(T_1)$; [c] the signal is observed above the temperature T; [d] ESR signal after transition of the compound to ferromagnetic state.

transfer from the donor to C_{60} (based on the number of $C_{60}^{-\bullet}$ spins per formula unit).[123, 127, 128]

d. X-ray photoelectron spectroscopy

X-Ray photoelectron spectroscopy (XPS) is a sensitive method for the determination of the valence state of elements in thin (0.5 – 4.0 nm) surface layers. Based on the position of lines corresponding to internal electronic shells of heteroatoms of the donors contained in the complex and their shift relative to the lines of the individual donor, it is possible to estimate the redistribution of the electron density upon formation of a D – A compound and the atomic composition of the compound.[200 – 205]

The C(1*s*) X-ray photoelectron spectrum of the C_{60} fullerene consists of the main singlet peak with an energy of 285 eV. The higher energy region contains a satellite shifted by 5.9 eV from the main C(1*s*) peak. It originates from excitation of a π-plasmon, *i.e.*, coordinated vibrations of π-electrons of the C_{60} molecules in a crystal.[206] The density of valence electrons is determined from the electron energy loss spectra (EELS). The loss function has two peaks in the case of the C_{60} fullerene,[203, 206] which correspond to the π-plasmon with a maximum at 5.8 eV originating from excitation of plasma vibrations of π-electrons and the (π + σ)-plasmon with a maximum at 26.1 eV originating from excitation of all valence electrons in C_{60}.[203, 206]

The position of the C(1*s*) peak in the XPS spectra of molecular complexes and salts of fullerenes remains unchanged, but some changes in its satellite structure occur.[44, 205] The disappearance of π – π* transitions of phenyl substituents of the donors in the satellite structure of C_{60} compounds, *e.g.*, in $(DAN)C_{60}(C_6H_6)_3$ [44] and in salts with bulky cations,[205] has been reported. This is due to the strong interaction of the phenyl substituents of the donor with the fullerene or to the fact that, upon formation of a compound with fullerene, the π – π* transitions in the donor molecule become less favourable than the excitation of plasma vibrations of π-electrons of the fullerene itself.[44, 205] In many compounds, a decrease in the energy of the π + σ-plasmon is observed: 24.0 eV in $(S_8)_2C_{60}$,[203] 25.2 eV in $(BTX)C_{60}(CS_2)$ [54, 119] and 25.5 eV in $TPDP(C_{60})_2(CS_2)_4$.[43]

The shift in the position of the S(2*p*), N(1*s*) and Te ($3d_{5/2}$) lines of the donor heteroatoms in various fullerene complexes by 0.1 – 1.0 eV towards higher energies can be caused [200, 201, 204] by the electron density shift from the donor to the fullerene. However, in some cases a similar shift in fullerene complexes in comparison with the individual donors can also be due to the calibration of spectra of the complex and the donor with respect to the C(1*s*) line, as the exact position of this line in the spectra of the donor and C_{60} can differ.[200] A shift in the position of the S(2*p*) peak in compound $(S_8)_2C_{60}$ towards lower energies by 0.4 eV has been reported.[203]

e. ^{13}C NMR spectroscopy

The ^{13}C NMR spectrum of crystalline C_{60} fullerene at room temperature contains a narrow singlet at δ 143.[29] This is caused by fast rotation of the C_{60} molecule and isotropic averaging of the signal. As the temperature is decreased, the rotation of fullerene molecules is hindered, and broadening of the signal is observed.[22] The observed phase transitions in fullerene at 255 and 90 K result in stepwise changes in the line width. The formation of molecular complexes does not change the position of the ^{13}C NMR signal of the fullerene.[93, 98, 114] The formation of fullerene anions, C_{60}^{n-} (n = 1, 2, 3), causes a shift of the ^{13}C NMR signal towards lower magnetic field, which can be due to the paramagnetic state of these ions.[50, 207, 208] However, the salts containing the $C_{60}^{-\bullet}$ and $C_{60}^{2-\bullet}$ anions have close chemical shifts of signals in the ^{13}C NMR spectra (δ 187 and 183, respectively), though their magnetic susceptibilities differ strongly.[207, 208] A shift of the ^{13}C NMR signal to δ 156 is also observed in the diamagnetic state of the C_{60}^{6-} anion.[208]

V. Conclusion

Based on the survey of the most important results concerning the synthesis and properties of the D – A complexes and radical ionic salts of fullerenes obtained over the last years, one can distinguish the most important directions of the development in this field and evaluate some possibilities of using fullerene compounds, both for obtaining new materials and for solving fundamental problems.

The ability of molecules of the C_{60} fullerene, its molecular complexes and salts to synchronise their rotation in crystals results in the appearance of unusual magnetic properties in these compounds. The existence of the frozen glassy magnetic state of fullerenes and molecular complexes of fullerenes with halogens has been established; radical anionic salts of $C_{60}^{-\bullet}$ with unsaturated amines possess ferromagnetic properties with the highest T_c among organic materials; various magnetic properties are displayed by complexes of C_{60} with metallocenes. Obviously, synthesis of D – A complexes of fullerenes with strong organic and organometallic donors, *viz.*, unsaturated amines, metallocenes and metalloporphyrins, and the study of their structure and properties will lead to new interesting results.

Another important direction includes the synthesis of conducting and superconducting materials based on fullerene compounds. By now, several dozens of superconductors with $T_c \leqslant 40$ K have already been obtained based on C_{60} and some specific features of their superconductivity have been rationalised. Superconducting phases can exist in fullerene compounds with alkali or alkaline-earth metals, lanthanides, and in salts of C_{60} with strong organic donors: they can be obtained both by direct chemical synthesis and by intercalation in the gas phase.

Fullerenes are weak acceptors, and the range of donors capable of reducing them to radical anions is limited. In addition, the essential drawback of both superconducting and ferromagnetic compounds of fullerenes is their instability in air. This restricts considerably the possibilities of obtaining and applying the fullerene-based materials with specific conducting and magnetic properties.

One possible way to solve these problems is the synthesis of three-component systems. The systems 'organic donor – fullerene radical anion – alkali metal cation' include a wider range of ionic compounds of fullerenes. In some of them, the fullerene radical anion can be stabilised because the bulky organic donor sterically hinders the approach of oxygen molecules to the fullerene radical anion.

In the majority of fullerene complexes that have been obtained, in particular in the complexes with tetrathiafulvalenes, charge transfer is insignificant because of the weak acceptor properties of C_{60} and C_{70}. However, in a three-component system 'donor radical cation – neutral fullerene – halide anion', fullerene compounds with radical cations of the donors can be obtained. Similar compounds can also possess conducting and magnetic properties.

Three-component systems can be obtained by intercalation of fullerene complexes (with either alkali metals or halogens) or by direct synthesis in solution. In the latter case, it is probably possible to obtain single crystals of these compounds.

Synthesis of complexes of chemically modified fullerenes, in particular, brominated, chlorinated and fluorinated ones, seems to be a promising direction. Unlike the C_{60} and C_{70} molecules, these derivatives have strong acceptor properties and can apparently yield molecular complexes and radical ionic salts with strong organic donors (*e.g.*, tetrathiafulvalenes).

The significant delocalisation of electrons in C_{60} upon photoinduced electron transfer results in the formation of free charge carriers and high photoconductivity. In the near future, this phenomenon can find application for the development of energy phototransducers and other devices that use photoconductivity. Therefore, the study of electron photoconduction in fullerene compounds is an important direction. The most promising compounds for the development of materials with high photo-

conductivity can include both the composites 'C_{60} – conducting polymer' and D – A complexes of fullerenes with organic donors, in which charge separation with significant life time is possible. The use of the combination 'organic donor – C_{60} – conducting polymer' is also promising.

The authors thank Yu M Shul'ga for useful discussions. The work has been carried out with financial support of the Russian programme 'Fullerenes and Atomic Clusters'.

References

1. H W Kroto, J R Heath, S C O Brien, R F Curl, R E Smalley *Nature (London)* **318** 162 (1985)
2. E Osawa *Kagaku (Kyoto)* **25** 854 (1970); *Chem. Abstr*. **74** 75 698 (1991)
3. D A Bochvar, E G Gal'pern *Dokl. Akad. Nauk SSSR* **209** 610 (1973) [a]
4. W Kratchmer, L D Lamb, K Fostiropoulos, D R Huffman *Nature (London)* **347** 354 (1990)
5. G Saito, T Teramoto, A Otsuka, Y Sugita, T Ban, M Kusunoki, K-i Sakaguchi *Synth. Met*. **64** 359 (1994)
6. C Brink, L H Andersen, P Hvelplund, D Mathur, J D Voldstad *Chem. Phys. Lett*. **233** 52 (1995)
7. R D Bolskar, R Mathur, C A Reed *J. Am. Chem. Soc*. **118** 13 093 (1996)
8. G Saito, F P Ferraris *Bull. Chem. Soc. Jpn*. **53** 2141 (1980)
9. R S Mulliken, W B Person *Molecular Complexes* (New York: Academic Press, 1969)
10. J M Williams, J R Ferraro, R J Thorn, K D Carlson, U Geiser, H H Wang, A M Kini, M-H Whangbo *Organic Superconductors (Including Fullerenes). Synthesis. Structure Properties and Theory*. (Englewood Cliffs, NJ: Prentice Hall, 1992)
11. R B Lyubovskii, R N Lyubovskaya, O A Dyachenko *J. Phys. I (France)* **6** 1609 (1996)
12. R C Haddon, A F Hebard, M J Rosseinsky, D W Murphy, S J Duclos, K B Lyons, B Miller, J M Rosamilia, R M Fleming, A R Kortan, S H Glarum, A V Makhija, A J Müller, R H Eick, S M Zahurak, R Tycko, G Dabbagh, F A Thiel *Nature (London)* **350** 320 (1991)
13. M J Rosseinsky *J. Mater. Chem*. **5** 1497 (1995)
14. K Tanigaki, K Prassides *J. Mater. Chem*. **5** 1515 (1995)
15. P W Stephens, D Cox, J W Lauher, L Mihaly, J B Wiley, P-M Allemand, A Hirsch, K Holczer, Q Li, J D Thompson, F Wudl *Nature (London)* **355** 331 (1992)
16. M Ricco, M Bisbiglia, R Derenzi, F Bolzoni *Solid State Commun*. **101** 413 (1997)
17. Y Wang *Nature (London)* **356** 585 (1992)
18. M Baenitz, M Heinze, K Luders, H Werner, R Schlogl, M Weiden, G Spain, F Steglich *Solid State Commun*. **96** 539 (1995)
19. H Kroto, J E Fischer, D E Cox *The Fullerenes* (Oxford: Pergamon Press, 1993)
20. C N R Rao, R Seshadri, A Govindaraj, R Sen *Mol. Sci. Eng*. **R15** 209 (1995)
21. V I Sokolov *Izv. Akad. Nauk SSSR, Ser. Khim*. 10 (1993) [b]
22. M S Dresselhaus, G Dresselhaus, P C Eklund *Science of Fullerenes and Carbon Nanotubes* (San Diego: Academic Press, 1996)
23. V I Sokolov, I V Stankevich *Usp. Khim*. **62** 455 (1993) [*Russ. Chem. Rev*. **62** 419 (1993)]
24. A V Eletskii, B M Smirnov *Usp. Fiz. Nauk* **163** 33 (1993) [c]
25. M S Dresselhaus, G Dresselhaus, P C Eclund *J. Mater. Res*. **8** 2054 (1993)
26. H Kuzmany, R Winkler, T Pichler *J. Phys., Condens. Matter* **7** 6601 (1995)
27. V Buntar, F M Sauerzopf, H W Weber *Aust. J. Phys*. **50** 359 (1997)
28. O Gunnarson *Rev. Mod. Phys*. **69** 575 (1997)
29. R D Johnson, D S Bethune, C S Yannoni *Acc. Chem. Res*. **25** 169 (1992)
30. R C Haddon *Acc. Chem. Res*. **21** 243 (1988)
31. D Dubois, K M Kadish, S Flanagan, R F Haufler, L P F Chibante, L J Wilson *J. Am. Chem. Soc*. **113** 4364 (1991)
32. W H Green Jr , S M Gorun, G Fitzgerald, P W Fowler, A Ceulemans, B Titeca *J. Phys. Chem*. **100** 14892 (1996)
33. C N R Rao, A Govindary, R Sumathy, A K Sood *Mol. Phys*. **89** 267 (1996).
34. N Liu, Y Morio, F Okino, H Touhara, O V Boltalina, V K Pavlovich *Synth. Met*. **86** 2289 (1997)
35. L Gherghel, M Baumgarten *Synth. Met*. **70** 1389 (1995)
36. M S Dresselhaus, G Dresselhaus, A M Rao, P C Eklund *Synth. Met*. **78** 313 (1996)
37. P A Heiney, J E Fischer, A R McGhie, W J Romanov, A M Denenstein, J P McCauley Jr , A B Smith III, D E Cox *Phys. Rev. Lett*. **67** 1468 (1991)
38. B Gotschy, R Gompper, H Klos, A Schilder, W Schutz, G Volkel *Synth. Met*. **77** 287 (1996)
39. R Blinc, D Arcon, K Pokhodnya *Synth. Met*. **85** 1713 (1997)
40. V Buntar, H W Weber, M Ricco *Solid State Commun*. **98** 175 (1995)
41. R H Michel, M M Kappers, P Adelmann, G Roth *Angew. Chem., Int. Ed. Engl*. **33** 1651 (1994)
42. A V Talyzin, V V Ratnikov, P P Syrnikov *Fiz. Tv. Tela* **38** 2263 (1996)
43. D V Konarev, O S Roschupkina, M G Kaplunov, Y M Shulga, E I Yudanova, R N Lyubovskaya *Mol. Mater*. **8** 83 (1996)
44. D V Konarev, E F Valeev, Yu L Slovokhotov, Y M Shulga, R N Lyubovskaya *J. Chem. Res. (S)* 442 (1997)
45. A Omerzu, D Mihailovic, S Tomic, O Milat, N Biscup *Phys. Rev. Lett*. **77** 2045 (1996)
46. A Suzuki, T Suzuki, Y Maruyama *Solid State Commun*. **96** 253 (1995)
47. A L Balch, J W Lee, B C Noll, M M Olmstead *Proc.-Electrochem. Soc*. **94-24** 1231 (1994); *Chem. Abstr*. **122** 133 376 (1995)
48. J Stinchcombe, A Penicaud, P Bhyrappa, P D W Boyd, C A Reed *J. Am. Chem. Soc*. **115** 5212 (1993)
49. P Bhyrappa, P Paul, J Stinchcombe, P D W Boyd, C A Reed *J. Am. Chem. Soc*. **115** 11 004 (1993)
50. P D W Boyd, P Bhyrappa, P Paul, J Stinchcombe, R D Bolskar, Y Sun, C A Reed *J. Am. Chem. Soc*. **117** 2907 (1995)
51. Y Sun, C A Reed *J. Chem. Soc., Chem. Commun*. 747 (1997)
52. R Ziebarth, S-M Lee, V A Stenger, C Pennington *Proc.-Electrochem. Soc*. **95-10** 316 (1995); *Chem. Abstr*. **124** 104 700 (1996)
53. C Janiak, S Muhle, H Hemling, K Kohler *Polyhedron* **15** 1559 (1996)
54. D V Konarev, R N Lyubovskaya, O S Roschupkina, Y M Shulga, M G Kaplunov, I N Kremenskaya, L P Rozenberg, S S Hasanov, R P Shibaeva *Mol. Mater*. **8** 79 (1996)
55. J Chen, Z Huang, R Cai, Q Shao, S Chen, H Ye *J. Chem. Soc., Chem. Commun*. 2177 (1994)
56. P-M Allemand, G Srdanov, A Koch, K Khemani, F Wudl, Y Rubin, F Diederich, M M Alvarez, S J Anz, R L Whetten *J. Am. Chem. Soc*. **113** 2780 (1991)
57. U Bilow, M Jansen *J. Chem. Soc., Chem. Commun*. 403 (1994)
58. H Moriyama, H Kobayashi *J. Am. Chem. Soc*. **115** 1185 (1993)
59. C A Foss, D L Feldman, D R Lawson, P K Dorhout, C M Elliott, C R Martin, B A Parkinson *J. Electrochem. Soc*. **140** l84 (1993)
60. H Kobayashi, H Moriyama, A Kobayashi, T Watanabe *Synth. Met*. **70** 1451 (1995)
61. H Moriyama, H Kobayashi, A Kobayashi, T Watanabe *Chem. Phys. Lett*. **238** 116 (1995)
62. W Bensch, H Werner, H Bartl, R Schlogl *J. Chem. Soc., Faraday Trans*. **90** 2791 (1994)
63. R S Ruoff, D S Tse, R Malhortra, D C Lorents *J. Phys. Chem*. **97** 3379 (1993)
64. N Sivaraman, R Dhamodaran, I Kaliappan, T G Srinivasan, P R V Rao, C K Mathews *Fullerene Sci. Technol*. **2** (3) 233 (1994)
65. M T Beck, G Mandi, S Keki *Proc.-Electrochem. Soc*. **95-10** 1511 (1995); *Chem. Abstr*. **124** 128 144 (1996)
66. S U Gallagher, R S Armstrong, P A Lay, C A Reed *J. Phys. Chem*. **99** 5817 (1995)
67. U Geiser, S K Kumar, B M Savall, S S Harried, K D Carlson, P R Mobley, H Hau Wang, J M Williams, R E Botto, W Liang, M-H Whangbo *Chem. Mater*. **4** 1077 (1992)
68. A L Balch, J W Lee, B C Noll, M M Olmstead *J. Chem. Soc., Chem. Commun*. 345 (1993)
69. M F Meidine, P B Hitchcock, H W Kroto, R Taylor, D R M Walton *J. Chem. Soc., Chem. Commun*. 1534 (1992)
70. S M Gorun, K M Creegan, R D Sherwood, D M Cox, V W Day, C S Day, R M Upton, C E Briant *J. Chem. Soc., Chem. Commun*. 1556 (1991)
71. M Ramm, P Luger, D Zjbel, W Duczek, J C A Boeyens *Cryst. Res. Technol*. **31** 43 (1996)

72. I I Gritsenko, O A D'yachenko, N D Kushch, N G Spitsina, E B Yagubskii, N V Avramenko, M N Frolova *Izv. Akad. Nauk, Ser. Khim.* 1248 (1994) [b]
73. T Arai, Y Murakami, H Suematsu, K Kikuchi, Y Achiba, I Ikemoto *J. Phys. Soc. Jpn.* **61** 1821 (1992)
74. A K Gangopadhyay, J S Schilling, M De Leo, W E Buhro, K Robinson, T Kowalewski *Solid State Commun.* **96** 597 (1995)
75. D V Konarev, R N Lyubovskaya, O S Roshchupkina, B P Tarasov, Yu M Shul'ga *Izv. Akad. Nauk, Ser. Khim.* 37 (1997) [b]
76. V A Nadtochenko, A A Moravsky, V V Gritsenko, G V Shilov, O A Dyachenko, in *Fullerenes and Atomic Clusters (IWFAC-95) (Abstracts of Reports), St.-Petersburg, 1995* p. 53
77. V A Nadtochenko, A A Moravsky, V V Gritsenko, G V Shilov, O A Dyachenko, in *Fullerenes and Atomic Clusters (IWFAC-95) (Abstracts of Reports), St.-Petersburg, 1995* p. 120
78. S Perkker, G Faigel, G Oszlayi, M Tegze, T Kemeny, E Jakab *Synth. Met.* **55–57** 3014 (1993)
79. R Ceolin, V Agafonov, B Bachet, A Gonthier, H Szware, S Toscani, G Keller, C Fabre, A Rassat *Chem. Phys. Lett.* **244** 100 (1995)
80. G Oszlanyi, G Bortel, G Faigel, S Pekker, M Tegze *J. Phys., Condens. Matter* **5** L165 (1993)
81. M Tegze, G Bortel, G Faigel, G Oszlanyi, S Pekker, P W Stefens *Nucl. Instrum. Methods Phys. Res. B* **97** 585 (1995)
82. E E Laukhina, Yu M Shul'ga, V I Zubtsov, V N Vasilets, V P Bubnov, E B Yagubskii, N V Avramenko, M N Frolova *Izv. Akad. Nauk, Ser. Khim.* 845 (1995) [b]
83. Z Yoshida, H Takehuma, S Takehuma, Y Matsubara *Agew. Chem., Int. Ed. Engl.* **33** 1597 (1994)
84. M Sundahl, T Anderson, O Wennerstroem *Proc.-Electrochem. Soc.* **94-24** 880 (1994); *Chem. Abstr.* **122** 251 785 (1995)
85. T Anderson, K Nelsson, M Sundahl, G Westman, O Wennerstrom *J. Chem. Soc., Chem. Commun.* 604 (1992)
86. J L Atwood, G A Koutsantonis, C L Raston *Nature (London)* **368** 229 (1994)
87. T Suzuki, K Nakashima, S Shinkai *Chem. Lett.* 699 (1994)
88. L J Barbour, G W Orr, J L Atwood *J. Chem. Soc., Chem. Commun.* 1439 (1997)
89. T Haino, M Yanase, Y Fukazawa *Agew. Chem., Int. Ed. Engl.* **36** 259 (1997)
90. G Roth, P Adelmann *Appl. Phys. A, Solids Surf.* **56** 169 (1993)
91. L I Buravov, O A D'yachenko, S V Konovalikhin, N D Kushch, I P Lavrent'ev, N G Spitsina, G V Shilov, E V Yagubskii *Izv. Akad. Nauk, Ser. Khim.* 262 (1994) [b]
92. H B Burgi, P Venugopalan, D Schwarzenbach, F Diederich, C Thilgen *Helv. Chim. Acta* **76** 2155 (1993)
93. R E Douthwaite, M L Green, S J Heyes, M J Rosseinsky, J F C Turner *J. Chem. Soc., Chem. Commun.* 1367 (1994)
94. P R Birkett, C Christides, P B Hitchcock, H W Kroto, K Prassides, R Taylor, D R M Walton *J. Chem. Soc., Perkin Trans. 2* 1407 (1993)
95. D V Konarev, E F Valeev, Yu L Slovokhotov, R N Lyubovskaya *J. Phys. Chem. Solids* **58** 1865 (1997)
96. M M Olmstead, A S Ginwalla, B C Noll, D S Tinti, A L Balch *J. Am. Chem. Soc.* **118** 7737 (1996)
97. N Sato, G Saito, H Inokuchi *Chem. Phys.* **76** 79 (1983)
98. A Izuoka, T Tachikawa, T Sugawara, Y Suzuki, M Konno, Y Saito, H Shinohara *J. Chem. Soc., Chem. Commun.* 1472 (1992)
99. S V Konovalikhin, O A D'yachenko, G V Shilov *Zh. Fiz. Khim.* **71** 2192 (1997) [d]
100. D V Konarev, Y V Zubavichus, Yu L Slovokhotov, Yu M Shul'ga, V N Semkin, N V Drichko, R N Lyubovskaya *Synth. Met.* **92** 1 (1998)
101. J Llacay, J Tarres, J Veciana, C Rovira *Synth. Met.* **70** 1453 (1995)
102. T Pradeep, K K Singh, A P B Sinha, D E Morris *J. Chem. Soc., Chem. Commun.* 1747 (1992)
103. P Wang, W-J Lee, I Scherbakova, M P Cava, R M Metzger *Synth. Met.* **64** 319 (1994)
104. D V Konarev, E F Valeev, Yu L Slovokhotov, Yu M Shul'ga, O S Roschupkina, R N Lyubovskaya *Synth. Met.* **88** 85 (1997)
105. D V Konarev, Yu M Shul'ga, O S Roschupkina, R N Lyubovskaya *J. Phys. Chem. Solids* **58** 1869 (1997)
106. Y Li, Y Gao, F Bai, Y Mo, B Zhang, H Han, D Zhu *Synth. Met.* **70** 1459 (1995)
107. S V Konovalikhin, O A D'yachenko, G V Shilov, N G Spitsina, K V Van, E B Yagubskii *Izv. Akad. Nauk, Ser. Khim.* 1480 (1997) [b]
108. T Suzuki, K Nakashima, S Shinkai *Chem. Lett.* 699 (1994)
109. B Zh Narymbetov, S S Khasanov, L V Zorina, L P Rozenberg, R P Shibaeva, D V Konarev, R N Lyubovskaya *Kristallografiya* **58** 851 (1997) [e]
110. A Izuoka, T Tachikawa, T Sugawara, Y Saito, H Shinohara *Chem. Lett.* 1049 (1992)
111. V V Kveder, E A Steinman, B Zh Narimbetov, S S Khasanov, L P Rozenberg, R P Shibaeva, A V Bazhenov, A V Gorbunov, M Yu Maksimuk, D V Konarev, R N Lyubovskaya, Yu A Ossipyan *Chem. Phys.* **216** 407 (1997)
112. Y Li, D Zhang, F Bai, D Zhu *Solid State Commun.* **86** 475 (1993)
113. A I Kotov, S I Konovalikhin,R I Pisarev, G V Shilov, O A Dyachenko, E B Yagubsky *Mendeleev Commun.* 180 (1994)
114. J W Steed, P C Junk, J L Atwood, M J Barnes, C L Raston, R S Burkhalter *J. Am. Chem. Soc.* **116** 10346 (1994)
115. L Y Chiang, J W Swirczewski, K Liang, J Miller *Chem. Lett.* 981 (1994)
116. M Fedurco, M M Olmstead, W R Fawcett *Inorg. Chem.* **34** 390 (1995)
117. A Graja, A Lapinski, S Krol *J. Mol. Struct.* **404** 147 (1997)
118. O Ermer *Helv. Chim. Acta* **74** 1339 (1991)
119. D V Konarev, R N Lyubovskaya, O S Roschupkina, Yu M Shul'ga, M G Kaplunov, I N Kremenskaya, L P Rozenberg, S S Hasanov, R P Shibaeva *Mendeleev Commun.* 3 (1996)
120. N S Sariciftci, L Smilowitz, A J Heeger, F Wudl *Science* **258** 1474 (1992)
121. C H Li, G Yu, D Moses, K Pakbaz, C Zhang, N,S Sariciftci, A J Heeger, F Wudl *Phys. Rev. B, Solid State* **48** 15425 (1993)
122. I I Khairullin, Y-H Chen, L-P Hwang *Chem. Phys. Lett.* **275** 1 (1997)
123. A Schilder, B Gotschy, A Seidl, R Gompper *Chem. Phys.* **193** 321 (1995)
124. H Wang, D Zhu *J. Phys. Chem. Solids* **55** 437 (1994)
125. H Wang, D Zhu, J Zhao, W Zhan *Synth. Met.* **70** 1471 (1995)
126. H Wang, D Zhu *Solid State Commun.* **93** 295 (1995)
127. H Klos, I Rystau, W Schutz, B Gotschy, A Skiebe, A Hirsch *Chem. Phys. Lett.* **224** 333 (1994)
128. A Skiebe, A Hirsch, H Klos, B Gotschy *Chem. Phys. Lett.* **220** 138 (1994)
129. V A Nadtochenko, V V Gritsenko, O A D'yachenko, G V Shilov, A P Moravskii *Izv. Akad. Nauk, Ser. Khim.* 1285 (1996) [b]
130. N F Gol'dshleger, A S Lobach, A S Astakhova, M G Kaplunov, A V Kulikov, A P Moravskii, O S Roshchupkina, Yu M Shul'ga *Izv. Akad. Nauk, Ser. Khim.* 1143 (1994) [b]
131. A S Lobach, N F Goldshleger, M G Kaplunov, A V Kulikov *Chem. Phys. Lett.* **243** 22 (1995)
132. F Wudl *Acc. Chem. Res.* **25** 157 (1992)
133. D Mihailovic, K Pokhodnya, A Omerzu, P Venturini, R Blink, P Cevc, F Pratt, K H Chow *Synth. Met.* **77** 281 (1996)
134. K Pokhodnia, J Bemsar, A Omerzu, D Mihailovic, H Kuzmany *Phys. Rev. B, Solid State* **55** 3757 (1997)
135. A Mrzel, P Cevc, A Omerzu, D Mihailovic *Phys. Rev. B, Solid State* **53** R2922 (1996)
136. K Yoshizawa, T Sato, K Tanaka, T Yamabe, K Okahara *Chem. Phys. Lett.* **213** 498 (1993)
137. R Tanaka, A A Zakhidov, K Yoshizava, K Okahara, T Yamabe, K Yakushi, K Kikuchi, S Suzuki, I Ikemoto, Y Achiba *Phys. Rev. B, Solid State* **47** 7554 (1993)
138. D Arcon, J Dolinsek, R Blink, K Pokhodnya, A Omerzu, D Mihailovic, P Venturini *Phys. Rev. B, Solid State* **53** 14028 (1996)
139. S Hino, K Umishita, H Iwasaki, K Tanaka, T Sato, T Yamabe, K Yoshizava, K Okahara *J. Phys. Chem., A* **101** 4346 (1997)
140. F Wudl, J D Thompson *J. Phys. Chem. Solids* **53** 1449 (1992)
141. B Gotschy, R Gompper, H Klos, A Seidl, A Schilder, W Schutz, G Volkel *Mol. Cryst. Liq. Cryst.* **272** 51 (1995)
142. K Tanaka, T Sato, T Kuga, T Yamabe, K Yoschizawa, K Okahara, A A Zakhidov *Phys. Rev. B, Solid State* **51** 990 (1995)
143. R Tanaka, A A Zakhidov, K Yoshizava, K Okahara, T Yamabe, K Kikuchi, S Suzuki, I Ikemoto, Y Achiba *Solid State Commun.* **85** 69 (1993)
144. J D Crane, P B Hitchcock *J. Chem. Soc., Dalton Trans.* 2537 (1993)

145. J D Crane, P B Hitchcock, H W Kroto, R Taylor, D R M Walton *J. Chem. Soc., Chem. Commun.* 1764 (1992)
146. A Otsuka, T Teramoto, Y Sugita, T Ban, G Saito *Synth. Met.* **70** 1423 (1995)
147. W Wang, Y L Lay, C Chang, H Chiu, K Chuang, B Wang *Synth. Met.* **86** 2293 (1997)
148. J P Selegue, S Dev, T F Guarr, J W Brill, E Figueroa *Proc.-Electrochem. Soc.* **94-24** 1245 (1994); *Chem. Abstr.* **122** 133 336 (1995)
149. W C Wan, X Liu, G M Sweeney, W E Broderick *J. Am. Chem. Soc.* **117** 9580 (1995)
150. M G Kaplunov, E V Golubeva, N G Spitsyna, E B Yagubskii, in *Fullerenes and Atomic Clusters (IWFAC-97) (Abstracts of Reports), St.-Petersburg, 1997* p. 37
151. C Bossard, S Rigaut, D Astruc, M-H Delvill, G Felix, A Fevrier-Bouvier, J Amiell, S Flandroids, P Delhaes *J. Chem. Soc., Chem. Commun.* 333 (1993)
152. V V Gritsenko, O A D'yachenko, G V Shilov, N G Spitsina, E B Yagubskii *Izv. Akad. Nauk, Ser. Khim.* 1982 (1997) [b]
153. A Penicaud, A Perez-Benitez, R Gleason V, E Munoz P, R Escudero *J. Am. Chem. Soc.* **115**10392 (1993)
154. A Penicaud, A Perez-Benitez, R Escudero, C Coulon *Solid State Commun.* **96** 147 (1995)
155. P Paul, Zuowei Xie, R Bau, P D W Boyd, C A Reed *J. Am. Chem. Soc.* **116** 4145 (1994)
156. A Penicaud, J Hsu, C A Reed, A Koch, K Khemani, P-M Allemand, F Wudl *J. Am. Chem. Soc.* **113** 6698 (1991)
157. S Pekker, L Granasy, G Oszlanyi, G Bortel, G Faigel, M Tegze, O Chauvet, L Forro, P W Stephens, A Janossy *Proc.-Electrochem. Soc.* **95-10** 244 (1995); *Chem. Abstr.* **124** 118 403 (1996)
158. F Bommeli, L Degiory, P Wacher, O Legeza, A Janossy, G Oszlanyi, O Chauet, L Forro *Phys. Rev. B, Solid State* **51** 14 794 (1995)
159. V Btouet, H Alloul, Y Yoshinary, L Forro *Phys. Rev. Lett.* **76** 3638 1996.
160. T T M Palstra, O Zhou, Y Imasa, P E Sulewski, R M Fleming, B R Zagarski *Solid State Commun.* **92** 71 (1994)
161. S Suzuki, V Nakao *Synth. Met.* **70** 1527 (1995)
162. H H Wang, J A Schluetter, A C Cooper, J L Smart, M E Whitten, U Geiser, K D Carlson, J M Williams, U Welp, J D Dudec, M A Caleca *J. Phys. Chem. Solids* **54** 1655 (1993)
163. H H Wang, A M Kini, B M Savall, K D Carlson, J M Williams, M W Lathrop, K R Lykke, D H Parker, P Wurz, M J Pellin, D M Gruen, U Welp, W-K Kwok, S Fleshler, G W Crabtree *Inorg. Chem.* **30** 2962 (1991)
164. X Lio, W C Wan, S M Owens, W E Broderick *J. Am. Chem. Soc.* **116** 5489 (1994)
165. J Mizuki, M Takai, H Takahashi, N Mori, K Tanigaki, I Hirisawa, K Prasides *Phys. Rev. B, Solid State* **50** 3466 (1994)
166. O Zhou, R M Fleming, D W Murphy, M J Rosseinsky, A P Ramirez, R B van Dover, R C Haddon *Nature (London)* **362** 433 (1993)
167. E Özdas, A R Kortran, N Kopylov, A P Ramirez, T Siegrist, K M Rabe, H E Bair, S Schuppler, P H Citrin *Nature (London)* **375** 126 (1995)
168. A Otsuka, G Saito, T Teramoto, Y Sunari, T Ban, A A Zakhidov, K Yakushi *Mol. Cryst. Liq. Cryst.* **284** 345 (1996)
169. A Otsuka, G Saito, A A Zakhidov, K Yakushi *Synth. Met.* **85** 1459 (1997)
170. Q Zhu, D E Cox, J E Fisher, K Kniaz, A R McGhie, O Zhou *Nature (London)* **355** 712 (1992)
171. L S Grigoryan, M Tokumoto *Solid State Commun.* **96** 523 (1995)
172. S Nakashima, M Noromoto, H Harima, Y Hamanaka, L S Grigoryan, M Tokumoto *Chem. Phys. Lett.* **268** 359 (1997)
173. R N Lyubovskaya, D V Konarev, E I Yudanova, O S Roschupkina, Yu M Shul'ga, V N Semkin, A Graja *Synth. Met.* **84** 741 (1997)
174. D V Konarev, R N Lyubovskaya, V N Semkin, A Graja *Pol. J. Chem.* **71** 96 (1997)
175. Yu L Slovokhotov, I V Moskaleva, V I Shil'nikov, E F Valeev, Yu N Novikov, A I Yanovsky, Yu T Struchkov *Mol. Mater.* **8** 117 (1996)
176. S Liu, Y J Lu, M M Kappes, J A Ibers *Science* **254** 408 (1991)
177. Y L Hwang, C C Yang, K C Hwang *J. Phys. Chem.* **101** 7971 (1997)
178. J Milliken, T M Keller, A P Baranovsky, S N McElvany, J H Callanhan, H H Nelson *Chem. Mater.* **3** 386 (1991)
179. H J Byrne, in *Progress in Fullerene Research* (Eds H Kuzmany, J Fink, M Mehring, S Roth) (Singapore: World Scientific, 1995) p. 183
180. S Leach, M Vervloet, A Despers, E Breheret, J P Hare, N J Dennes, H W Kroto, R Taylor, R M Walton *Chem. Phys.* **160** 451 (1992)
181. D V Konarev, V N Semkin, R N Lyubovskaya, A Graja *Synth. Met.* **88** 225 (1997)
182. S P Sibley, R L Campbell, H B Silber *J. Phys. Chem.* **99** 5274 (1995)
183. R D Scurlock, P R Ogilby *J. Photochem. Photobiol. A, Chem.* **91** 21 (1995)
184. V N Semkin, N G Spitsina, S Krol, A Graja *Chem. Phys. Lett.* **256** 616 (1996)
185. K Kamaras, A Breistchwerdt, S Pekker, K Fodor-Csorba, G Faigel, M Tegze *Appl. Phys. A, Solid Surf.* 231 (1993)
186. M C Martin, X Du, J Kwon, L Mihaly *Phys. Rev. B, Solid State* **50** 174 (1994)
187. V N Semkin, N G Spitsina, A Graja *Chem. Phys. Lett.* **233** 291 (1995)
188. K Kamaras, V G Hadjiev, C Thomsen, S Pekker, K Fodor-Csorba, G Faigel, M Tegze *Chem. Phys. Lett.* **202** 325 (1993)
189. L R Narasimhan, D N Stoneback, A F Hrbard, R C Haddon, C K N Patel *Phys. Rev. B, Solid State* **46** 2591 (1992)
190. A V Bazhenov, M Yu Maksimuk, T N Fursova, A P Moravskii, V A Nadtochenko *Izv. Akad. Nauk, Ser. Khim.* 1459 (1996) [b]
191. T Picher, R Winkler, H Kuzmany *Phys. Rev. B, Solid State* **49** 15879 (1994)
192. R Winkler, H Kuzmany *Solid State Commun.* **84** 935 (1992)
193. V E Kampar, I Ya Gudele, R B Kampare, S P Valtare, O Ya Neiland *Zh. Obshch. Khim.* **51** 2553 (1980) [f]
194. N D Kushch, I Majchrzak, W Ciesielski, A Graja *Chem. Phys. Lett.* **215** 137 (1993)
195. K Kamaras, K Matsumoto, M Wojnowski, E Schonherr, H Klos, B Gotschy, in *Progress in Fullerene Research* (Eds H Kuzmany, J Fink, M Mehring, S Roth) (Singapore: World Scientific, 1994) p. 357
196. M D Pace, T C Christidis, J J Yin, J Millikin *Phys. Chem.* **96** 6858 (1992)
197. J Stankowski, P Byszewski, W Kempinski, Z Trybuka, N Zuk *Phys. Stat. Solids, B* **178** 221 (1993)
198. M C Martin, D Koller, L Mihaly, S Pekker *Proc.-Electrochem. Soc.* **94-24** 608 (1994); *Chem. Abstr.* **122** 115 471 (1995)
199. G Volkel, A Poppl, J Simon, J Hoentsch, S Orlinskii, H Klos, B Gotschy *Phys. Rev. B, Solid State* **52** 14028 (1995)
200. Yu M Shul'ga, R N Lyubovskaya, D V Konarev *Phys. Low-Dim. Struct.* **1/2** 103 (1997)
201. Yu M Shul'ga, V I Rubtsov, N G Spitsyna, Ya L Kogan *Synth. Met.* **86** 2359 (1997)
202. H A Romberg, M Knupfer, J F Armbruster, G Roth *Synth. Met.* **70** 1379 (1995)
203. Yu M Shul'ga, V I Rubtsov, V N Vasilets, A S Lobach, N G Spitsyna, E B Yagubskii *Synth. Met.* **70** 1381 (1995)
204. Yu M Shul'ga, R N Lyubovskaya, D V Konarev *Zh. Fiz. Khim.* **71** 2188 (1997) [d]
205. Yu M Shul'ga, N G Spitsina, E B Yagubskii *Dokl. Akad. Nauk* **348** 502 (1996) [a]
206. Yu M Shul'ga, V I Rubtsov, A S Lobach *Z. Phys., B* **93** 327 (1994)
207. R E Douthwaite, A R Brough, M L H Green *J. Chem. Soc., Chem. Commun.* 267 (1994)
208. J Chen, Z Huang, R Cai, Q Shao, H Ye *Solid State Commun.* **95** 233 (1995)

[a] — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*
[b] — *Russ. Chem. Bull. (Engl. Transl.)*
[c] — *Physics-Uspekhi (Engl. Transl.)*
[d] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[e] — *Russ. Crystallography (Engl. Transl.)*
[f] — *Russ. J. Gen. Chem. (Engl. Transl.)*