Russian Chemical Reviews **81** (4) 336 – 366 (2012) © 2012 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2012v081n04ABEH004273

Molecular design, study of the structures and properties of ionic fullerene compounds

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Abstract. The results of studies devoted to ionic compounds of fullerenes, which are of interest for the design of new materials with promising physical properties, are analyzed. The preparation methods of these compounds and their electrophysical, magnetic and optical properties, and the molecular and electronic structures of monomeric, dimeric and polymeric fullerene anions are considered. The results of investigations of fullerenes in various charge states by electronic, IR, EPR and ^{13}C NMR spectroscopies are presented. The bibliography includes 266 references.

I. Introduction

Fullerenes are carbon allotropes consisting of polyhedral molecules where faces are formed by five- and six-membered rings (Fig. 1). The simplest available fullerene is C_{60}. Its molecule has an icosahedral symmetry (I_h group) and its truncated icosahedral cage comprises 20 hexagonal and 12 pentagonal faces.[3] The next in size is C_{70} fullerene. Its molecule can be constructed by adding five hexagonal faces to the equatorial plane of the C_{60} molecule; C_{70} has an oblong shape and a lower D_{5h} symmetry (see Fig. 1). Higher fullerene cages (C_{76}, C_{78}, C_{84}, *etc.*) can also be constructed by adding hexagonal faces to the surface of highly symmetric C_{60} molecule, resulting in further reduction of the symmetry (for example, C_{84}, see Fig. 1). In the early 1990s, methods for the preparation of gram amounts of C_{60} and C_{70} fullerenes were developed;[4] higher fullerenes (starting from C_{76}) are still poorly accessible and are used only in milligram quantities.

Fullerenes exhibit electron-withdrawing properties; they can be considered as three-dimensional π-acceptors composed of only carbon atoms.[5] Similarly to planar organic π-acceptors, such as tetracyanoquinodimethane (TCNQ), tetracyanoethylene (TCNE), *p*-benzoquinone and so on, they form a broad range of donor – acceptor complexes and radical ion salts with electron donors. An important factor determining the conductive and magnetic properties of these compounds is their radical-ion nature caused by either partial or complete electron transfer from the donor to the acceptor.

Upon special structural design and selection of components affecting the degree of charge transfer, complexes based on π-donors and π-acceptors can acquire unique conductive and magnetic properties. Indeed, ionic compounds of sulfur- and selenium-containing organic heterocycles (so-called organic metals) demonstrate metallic conductivity and superconductivity; they may combine ferromagnetism with metallic conductivity or optical activity with metallic properties.[6–8] The discovery of fullerenes provided researchers with novel π-acceptors having large size, quasispherical shape, unique electronic structure and

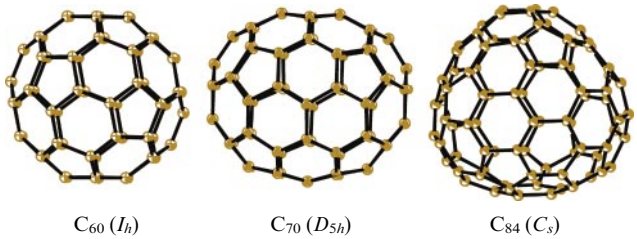


Figure 1. Molecular structures and symmetry of some fullerenes.[1,2]

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Received 27 September 2011
Uspekhi Khimii **81** (4) 336 – 366 (2012); translated by Z P Svitanko

Table 1. Vertical electron affinities (EA), reduction potentials (E_{red}) and oxidation potentials (E_{ox}) of fullerenes.

Fullerene	EA /eV	Ref.	Reduction potentials /V				Ref.	E^1_{ox} /V	Ref.
			E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}			
C_{60}	2.666 ± 0.001	38	-0.49 [a]	-0.88 [a]	-1.38 [a]	-1.86 [a]	13	1.75 [b]	39
			-0.442 [c]	–	–	–	5	–	–
C_{70}	2.75 ± 0.01	40	-0.48 [a]	-0.85 [a]	-1.29 [a]	-1.72 [a]	13	1.69 [b]	39
C_{76}	2.90 ± 0.02	40	-0.34 [a]	-0.68 [a]	-1.19 [a]	-1.61 [a]	41	1.30 [b]	42
C_{84}	3.15 ± 0.04	40	-0.18 [b]	-0.51 [b]	-0.85 [b]	-1.23 [b]	42	1.42 [b]	42

[a] The data were obtained in MeCN – PhMe (1 : 5.4 by volume) *vs.* ferrocene reference electrode (Fc/Fc^+), 0.1 M $Bu^n_4NPF_6$; [b] the data were obtained in $CHCl_2CHCl_2$ *vs.* Fc/Fc^+; [c] the data were obtained in MeCN *vs.* SCE. The conversion factor between Fc/Fc^+ and SCE is 0.49 V.

high polarizability. Compounds with unique physical properties were prepared based on C_{60} fullerene. It was found, for example, that intercalation of alkali metals into C_{60} produces superconductors M_3C_{60} (M = K, Rb, Cs) with rather high superconducting transition temperatures (T_c) ($18 \leqslant T_c \leqslant 40$ K).[9,10] The radical ion salt of C_{60} with the organic donor TDAE [tetrakis(dimethylamino)ethylene] is a purely organic ferromagnet with the highest Curie temperature known for an organic material ($T_C = 16$ K).[11] In compounds of C_{60} with cerium Ce_xC_{60}, superconductivity coexists with ferromagnetism.[12]

Quite a few charge transfer complexes and radical ion salts of fullerenes with diverse charge states of fullerene molecules have been prepared to date. The charge states of C_{60} may vary over a broad range: this molecule can accept up to 12 electrons [13,14] and give off up to two electrons.[15] The fullerene anions and cations can dimerize and polymerize, thus yielding unusual σ-bonded structures.[16] All this accounts for the high diversity of both the structure and the properties of fullerene compounds.

The great interest in the fullerenes and compounds based on them is reflected in the enormous number of relevant books and reviews.[17–36] In particular, detailed accounts were given of the general properties,[17–20] spectroscopy [20–22] and chemistry of fullerenes;[23–29] magnetic [30,31] and conductive [32] characteristics of fullerenes and their compounds; intercalation of alkali and alkaline earth metals and lanthanides [14,33] into fullerenes; the properties of fulleride anions;[34] and coordination compounds of fullerenes.[35,36] In 1999, we published a review dealing with the donor–acceptor and ionic fullerene compounds.[37] Over the last 12 years, considerable progress was made in the field of ionic compounds of fullerenes, a large number of new compounds was obtained, and their structures and physical properties were studied.

This review considers the up-to-date knowledge concerning the synthesis and study of ionic compounds of fullerenes with organic, organometallic donors and cations. This includes the preparation methods of ionic fullerene compounds, their conductive, magnetic and optical properties; the molecular and electronic structures of monomeric, dimeric and polymeric fullerene anions; and results of fullerene investigations in various charge states by UV/Vis, IR and ^{13}C NMR spectroscopy and EPR.

II. Acceptor and donor properties of fullerenes

The cyclic voltammogram of C_{60} exhibits six electrochemically reversible reduction waves up to the formation of the hexaanion (Table 1 lists the first four potentials).[13] The acceptor nature of C_{60} fullerene is indicated by the value of the first reduction potential, which is only -0.49 V in a MeCN – PhMe mixture *vs.* SCE. The first reduction potential of C_{60} (-0.442 V, MeCN, SCE) is shifted by 0.6–0.7 V to the negative region with respect to the potentials of organic π-acceptors, TCNQ ($+0.222$ V) and TCNE ($+0.286$ V), measured under the same conditions [5] and is similar to the potentials of relatively weak acceptors such as 2,5-dibromo-*p*-xyloquinone (-0.318 V) and *p*-benzoquinone (-0.456 V). Fullerene C_{70} has nearly the same first reduction potential; however, for higher fullerenes, the potentials are shifted considerably to positive values, *i.e.*, they are stronger acceptors (see Table 1). The reduction potentials of fullerenes for different charge states are separated by about 0.30–0.45 V. This difference is observed for all fullerenes being retained up to the sixth potential. A change in the solvent polarity slightly shifts the potential of C_{60}, which is -0.31 V in polar DMF and ~ -0.58 V in low-polarity chloro- and bromobenzenes (*vs.* the $Me_{10}Fc/Me_{10}Fc^+$ reference electrode).[43,44]

The electron affinities (EA) [38,40] and ionization potentials [45] of fullerenes in the gas phase have been estimated. The gas-phase electron affinities of C_{60} and C_{70} fullerenes are rather high (2.66–2.75 eV) but the adiabatic EA of C_{60} and C_{70} in solution found from the charge transfer energy and the redox potentials are much smaller being equal to 2.10–2.20 eV.[5,46] This value is much lower than the electron affinities of TCNQ (2.82 eV) and TCNE (2.90 eV) and is comparable with the electron affinities of 2,5-dibromo-*p*-xyloquinone (2.19 eV) or 1,2,3,4-tetracyanobenzene (2.15 eV).[5] Thus, although being acceptors, fullerenes show rather weak electron-withdrawing properties. Higher fullerenes, which have higher electron affinities, are thus stronger acceptors (see Table 1).[40,45]

A possible way of increasing the EA is the addition of electron-withdrawing addends such as halogens, cyano groups, trifluoromethyl groups to the fullerene cage (Fig. 2). Indeed, it was shown [50,51] that halogenated fullerenes exhibit stronger electron-withdrawing properties than C_{60}. For $C_{60}Br_8$ (see Fig. 2), theoretical calculation gives EA of ~ 4.0 eV.[50] The electron affinities of the $C_{60}F_{36}$ and $C_{60}F_{48}$ molecules are also higher than that of C_{60} (3.48 and 4.06 eV, respectively).[51] Fluorinated $C_{60}F_{36}$, $C_{60}F_{48}$ and $C_{70}F_{54}$ fullerenes have much more positive first reduction potential (-0.05, 0.555 and 0.805 V, respectively, *vs.* SCE in dichloromethane) than the corresponding parent fullerenes.[51] However, ionic compounds with halofullerenes have not been obtained as yet. The first studies that

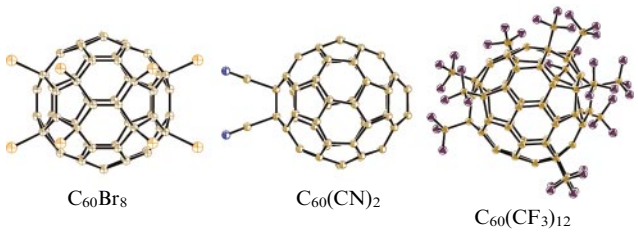


Figure 2. Substituted fullerenes exhibiting acceptor properties: $C_{60}Br_8$,[47] $C_{60}(CN)_2$ (Ref. 48) and $C_{60}(CF_3)_{12}$.[49]

reported the formation of the ionic compound $(TTF)_x(C_{60}Br_8)$ (TTF is tetrathiafulvalene) proved faulty.[50] Actually, in the presence of a donor, the halofullerene anion splits off halogen atoms to give the corresponding salt, for example, $(TTF^+)Br^-$, and the parent non-modified fullerene.[52] This type of reaction is observed for not only halofullerenes $C_{60}Cl_6$ and $C_{60}Br_8$ [52] but also for halofullerenes with more substituents ($C_{60}Cl_{24}$ and $C_{60}Cl_{30}$).[53]

Cyanofullerenes are promising acceptors (see Fig. 2). Dicyanofullerene has the first reduction potential (-0.935 V *vs.* Fc/Fc^+) more positive than the potential of C_{60} measured under the same conditions (-1.056 V) and can be reduced up to the tetraanion without elimination of cyano groups.[48] Several ionic compounds of dicyanofullerene have been obtained;[54,55] they are considered below. However, many organic donors, for example, substituted tetrathiafulvalenes, fail to reduce dicyanofullerene to the radical anion. An increase in the number of cyano groups on the fullerene cage could enhance the electron-withdrawing properties of fullerene but these compounds have not been isolated in macro quantities, as even the preparation of tetracyanofullerene affords an isomer mixture that is difficult to separate.[56]

Cyanofullerenes can be synthesized by replacing halogen atoms in chlorofullerenes. For example, $C_{60}Cl_6$ was converted to the very stable $C_{60}(CN)_5^-$ anion resistant to oxidation in air.[57] However, the negative charge of $C_{60}(CN)_5^-$ is concentrated in the five-membered ring surrounded by cyano groups rather than on the whole fullerene cage, and this anion is diamagnetic; to acquire the negative charge on the fullerene sphere, further reduction to the dianion is required. Numerous fullerenes with trifluoromethyl addends have been prepared (see Fig. 2). They are stable against reduction, and many trifluoromethyl derivatives are stronger as acceptors than the parent fullerene [58] but no ionic compounds have been obtained with them as yet.

Fullerenes, especially C_{60}, have very high oxidation potentials (see Table 1). An EPR study demonstrated the formation C_{60} radical cations in solutions with potent oxidants,[59] but individual compounds with positively charged C_{60} were not isolated for a long time. Only recently, did oxidation of C_{60} fullerene give the first ionic compound $C_{60}^{2+}(SbF_6^-)_2$ with the fullerene dication.[60] One cationic compound of C_{70} with a complex titanium anion is known, namely, $(C_{70}^+)_2(Ti_3Cl_{13}^-)_2$ (Ref. 61). The fullerene C_{76} and other higher fullerenes are oxidized somewhat more easily than C_{60}. For example, C_{76} is oxidized by a tris(2,4-dibromophenyl)ammonium cation ($E_{red} = 1.16$ V, the $CB_{11}H_6Br_6^-$ counter-ion) to give a radical cation salt with a positive charge on the fullerene sphere.[15]

III. Preparation of ionic compounds of fullerenes in solution

1. Stability of fullerene anions

As noted above, the reduction potentials of fullerenes to different anionic states are separated by 0.30–0.45 V; hence, it is rather easy to select the appropriate reducing agents for the selective preparation of the fullerene anion with the desired charge in solution. Considerable complications in the study of fullerene anions come from their oxygen sensitivity due to the possible reaction

$$C_{60}^{n-} + nO_2 \longrightarrow C_{60} + nO_2^-.$$

The reaction can also give peroxide anions $C_{60}O_2^-$, which are formed upon the addition of oxygen to a [6,6]- or [6,5]-bond of fullerene.[62]

In aprotic media, the reduction potential of the O_2/O_2^- pair is -0.8 V,[63] while the first potential of C_{60}/C_{60}^- and C_{70}/C_{70}^- is about -0.4 V.[64] At these potentials, the oxidation of the C_{60}^- and C_{70}^- anions is thermodynamically unfavourable, and compounds with these anions should be air-stable. Indeed, some salts (KC_{60}, RbC_{60}, CsC_{60} and salts with bulky cations) are air-stable in the solid state.[65–67] Meanwhile, the salts C_{60}^- in solution and the solid fullerene salts with metal porphyrins,[68] metallocenes [63] and amines [11] are rapidly oxidized in air. This may be due to stabilization of O_2^- by a proton or a metal cation. The potential of the O_2/O_2^- pair becomes more positive, which enables the oxidation of C_{60}^-. Fullerenes with a charge of -1 are rather resistant to water. There are even publications in which the $C_{60}^{-\bullet}$ and $C_{70}^{-\bullet}$ radical anions were generated in water in the presence of alkali.[69]

The second reduction potential in the C_{60}^-/C_{60}^{2-} and C_{70}^-/C_{70}^{2-} systems is ~ -0.8 V,[64] so the oxidation of fullerene dianions with oxygen is thermodynamically favourable. Therefore, the fullerene dianions and C_{60}^{n-} anions at more reduced states are highly sensitive to oxygen.[70] The basicity of more reduced fullerenes considerably increases, being seven orders of magnitude higher for the C_{60}^{2-} dianion than for the $C_{60}^{-\bullet}$ radical anion (the pK_a values differ by 7 units);[71] the fullerene anions in more reduced states are even stronger bases.[72] The dianions are very sensitive to even traces of water.

Since ionic fullerene compounds in solutions are sensitive to water and oxygen traces, they are to be handled under inert atmosphere with oxygen and water contents of < 1‰ using thoroughly dehydrated solvents.

2. Reagents for fullerene reduction

a. Alkali metals

Alkali metals can be used to prepare fullerene salts with charges of up to -6 in solutions; the key challenge in this reduction is the process selectivity. A good method for selective reduction of fullerene C_{60} is the procedure proposed by Reed,[63,70,72,73] who employed stoichiometric amounts of crown ethers or cryptands and an excess of alkali metal in tetrahydrofuran. Salts with fullerene anions up to the tetraanion were obtained in this way; then these salts can be converted to salts with bulky cations [for instance, bis(triphenylphosphoranylidene)ammonium, PPN^+] by cation metathesis in acetonitrile.[70,73]

A similar method for the preparation of salts with fullerene anions C_{60}^{2-} and C_{60}^{3-} was used by Fässler's

group;[74–76] the reduction was carried out in dimethylformamide and the degree of fullerene reduction was controlled by using appropriate amounts of crown ether or cryptand. The salts thus obtained were crystallized by diffusion of toluene or THF into a salt solution in DMF.

Compounds of fullerenes with alkali metals, $M_xC_{60}^{x-}(THF)_y$ ($x = 0.4, 1, 2, 3$; $y = 1-14$), can be prepared by the reaction of C_{60} with alkali metal in THF with addition of 1-methylnaphthalene, which is reduced by the alkali metal and thus transfers electron from the alkali metal to fullerene;[77,78] by cooling a solution of C_{60} reduced by potassium in tetramethylethylenediamine;[79] by the reduction of fullerene with alkali metal in the presence of a large crown ether (dibenzo-24-crown-8 is not incorporated in the salt due to weak binding with the metal cation);[80] by the reaction of C_{60} with $K[MnCp^*_2]$ ($Cp^* = \eta^5$-C_5Me_5) in toluene or THF.[81,82] The reduction of fullerene with excess lithium in THF in the presence of corannulene affords diamagnetic products presumably containing C_{60}^{6-} and C_{70}^{6-} hexaanions.[83] Salts with a non-stoichiometric content of the metal cation, $M_xC_{60}(THF)_y$ (M = Li, Na, K; $x \approx 0.4$; $y \approx 2.2$), were prepared using alkali metal tetraphenylborates. This reaction was initially performed electrochemically but later it was found that the tetraphenylborate anion can itself reduce fullerene when a THF solution of tetraphenylborate of the corresponding metal is diffused into a solution of C_{60} in chlorobenzene.[84–86] Other solvents that solvate metal cations, for example, *N*-methylimidazole (MeIm),[87] liquid ammonia[88–90] or methylamine,[10] are also suitable for the preparation of fullerene salts with alkali metals.

Other metals such as Ca, Ba, Fe, Cu and Zn can also be used for fullerene reduction. Heating and stirring of a suspension of fullerene in MeIm with a large excess of metal (Ca, Ba, Fe, Cu, Zn) gave salts of $C_{60}^{-\bullet}$ and C_{60}^{2-} of the composition $[M(MeIm)_x]C_{60}$ and $[M(MeIm)_x]_2C_{60}$ ($x = 4-6$).[87] Alkaline earth metals (Mg, Ca),[91,92] sodium amalgam in toluene,[92] Eu,[93] Hg,[92,94–96] a nickel–aluminium alloy[69,97] can also be used for the reduction of fullerene.

b. Organometallic and organic compounds

Organometallic compounds are successfully used to prepare ionic compounds of fullerenes with the charge of -1, -2 and -3 in solutions. Table 2 summarizes the redox potentials of some of these compounds. The most potent donors are the salt $K[MnCp^*_2]$ and the compounds $Fe^{I}Cp(C_6Me_6)$ ($Cp = \eta^5$-C_5H_5) and $Co^{II}Cp^*_2$, which generate even fullerene trianions in solution, although most donors produce only the C_{60}^{-} monoanions.

The redox potentials of metallocenes depend only slightly on the solvent polarity; therefore, metallocenes generate the fullerene anions both in polar and non-polar media. However, metal porphyrins produce fullerene anions only in the presence of coordinating solvents, which stabilize the resulting cation, for example, $Cr^{III}TPP^+$, whereas fullerene is a too weak ligand unable to stabilize the metal cation of metal porphyrin.

In some cases, the reduction of fullerenes by metallocenes can be accompanied by the reduction–addition reaction (see Table 2). For example, according to its redox potential, chromocene can reduce fullerene to a radical anion. Indeed, in benzonitrile in the presence of excess

Table 2. Redox properties of the donors used to prepare ionic complexes with fullerenes.

Compound	Potential *vs.* SCE /V	Charge of the C_{60} anion	Ref.
$K[MnCp^*_2]$	−2.17	−1, −2, −3	81, 82
$Fe^{I}Cp(C_6Me_6)$	−1.55	−1, −2, −3	98
$Co^{II}Cp^*_2$	−1.55	−1, −2, −3	70
$Ru^0(bipy)_3$	−1.40 [a]	−1, −2	99
$Cr^{II}Cp^*_2$	−1.04	−1, −2	100, 101
$Co^{II}Cp_2$	−0.91	−1, −2	63, 101, 102
$Cr^{II}TPP$	−0.86	−1	68
TDAE	−0.75	−1	11
$Cr^0(C_6H_6)_2$	−0.72	−1	101, 103
$Cr^0(MePh)_2$		−1	104, 105
$Ni^{II}Cp^*_2$	−0.65	−1	106
$Mn^{II}Cp^*_2$	−0.55	−1	87
$Cr^{II}Cp_2$	−0.55	−1 (see [b])	101

Notes. bipy is 2,2′-bipyridine, TPP is the 5,10,15,20-tetraphenylporphyrin dianion. [a] The potential was measured *vs.* Fc/Fc^+ and converted to SCE. [b] Addition takes place simultaneously.

$CrCp_2$, absorption bands of $C_{60}^{-\bullet}$ appear and then disappear after 3 h (Fig. 3). Apparently, the first fast step is the reduction giving two ions, $(CrCp_2)^+$ and $C_{60}^{-\bullet}$, and the next slower step includes the η^2-coordination of $(CrCp_2)^+$ to $C_{60}^{-\bullet}$ to give the $(CrCp_2)^+(C_{60}^{-\bullet})$ zwitter-ion, and this gives rise to a new broad spectral band at 1000 nm. The intensity of this band decreases with time, probably due to recombination of radicals in the zwitter-ion to give a neutral coordination compound, η^2-$CrCp_2(C_{60})$.[101] Vanadocene[107] and titanocene[108] also add to fullerene to give the coordination compounds η^2-$MCp_2(C_{60})$ (M = Ti, V).

Some organic compounds are also suitable for the reduction of fullerenes. For example, in the presence of potassium carbonate, propanethiol can reduce fullerene, depending on the solvent, to -1 (benzene–DMSO) or -2 (DMSO).[109] Subsequently, this procedure was modified to enable selective preparation of the C_{60}^{2-} dianion in acetoni-

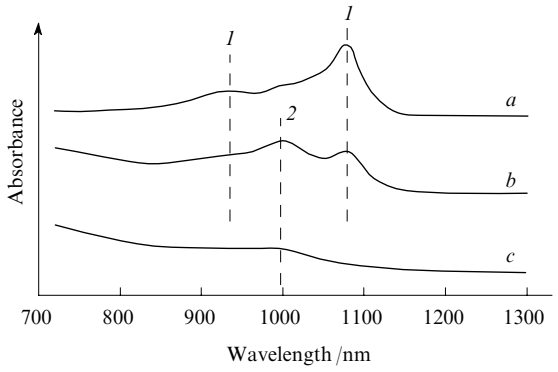


Figure 3. IR spectrum of a benzonitrile solution containing C_{60} and $CrCp_2$ in 1 : 10 molar ratio at different time periods after preparation: 2 min (*a*), 1.5 h (*b*), 3 h (*c*).[101]
The bands assigned to $C_{60}^{-\bullet}$ (*1*) and the $(CrCp_2)^+C_{60}^{-\bullet}$ zwitter-ion (*2*) are marked.

trile; this was done using commercially available sodium ethanethiolate.[110] The possibility of reducing fullerene with hydrogen sulfide anion in the basic medium was also demonstrated.[69, 111]

Some primary amines (3-aminopropanol, 1,5-diaminopentane) can also generate −1- and even −2-charged C_{60} and C_{70} anions.[112, 113] Also, it was noted that the addition of methoxide [114] or hydroxide anions [115] to C_{60} is accompanied by the formation of the $C_{60}^{-\bullet}$ radical anions in solutions. The process mechanism can be described in the following way. The addition of these anionic species to fullerene yields the corresponding $MeOC_{60}^-$ and HOC_{60}^- anions. The disruption of electron density delocalization makes these anions more potent donors as compared with the $C_{60}^{-\bullet}$ radical anion, and hence, they can reduce the initial fullerene to the radical anion state. Thus, although MeO^- and HO^- lack donor properties sufficient for the reduction of fullerenes, they are able to generate fullerene radical anions in solutions *via* the addition step.

c. Cation metathesis

The fullerene salts with alkali metals are also prepared by gas-phase doping of fullerenes. These salts (for example, K_2C_{60}, K_2C_{70}, *etc.*) are soluble in organic solvents and can be used in cation metathesis reactions. The polymeric salts MC_{60} are insoluble in organic solvents; in this case, the soluble salt $\{K^+(THF)_5\}C_{60}^{-\bullet}$ can be used.[116] The metathesis is carried out in liquid ammonia or in acetonitrile. A large series of salts was obtained containing fullerene anions, C_{60}^{2-}, C_{70}^{2-} and C_{70}^{3-}, and a transition metal cations solvated by ammonia [$M^{2+}(NH_3)_x$, M = Ni, Mn, Co, Zn, Cd, Sr, Ba; $x = 6-8$] or a benzyltrimethylammonium cation.[117–124] The cation metathesis of Rb_3C_{60} with the salts Me_4NCl, Et_4NBr and Me_4PCl in liquid ammonia gives the salts $(Ct^+)_3(C_{60}^{3-})$ (Ct is cation); the products were isolated as powders.[125] Another example of cation metathesis is the exchange of $K^+(THF)_5$ with the tetramethylammonium cation in acetonitrile at −30 °C. After the exchange reaction, the salt was dissolved in THF, and the crystals of $(Me_4N)C_{60}\cdot 1.5\,THF$ were precipitated with hexane from a concentrated solution.[116] Worthy of note is also the versatile method for the preparation of the $C_{60}^{-\bullet}$ salts by the reduction of parent fullerene in THF or benzonitrile with mercury in the presence of methylpyridinium, tetraalkylammonium and tetraalkylarsonium bromides. The reduction is accompanied by cation metathesis, the insoluble Hg_2Br_2 salt precipitates, only the $C_{60}^{-\bullet}$ salt with a minor impurity of C_{60}^{2-} remaining in the solution.[94–96]

We developed a procedure for preparing fullerene salts by the cation metathesis reaction with various organic cations (Fig. 4).[126–129] In the first stage, fullerene is reduced with sodium ethanethiolate in the presence of excess Ct^+X^- (X = I, Br or Cl) in a *o*-$Cl_2C_6H_4$–PhCN mixture (14 : 2). The fullerenes C_{60} and C_{70} are reduced under these conditions to monoanions. The salts NaX and EtSNa are poorly soluble in this medium and can be filtered off after the reduction (1–2 h), whereas the soluble salts $Ct^+C_{60}^{-\bullet}$ can be further precipitated from the solution as crystals at hexane diffusion. The reduction of fullerenes with excess EtSNa in pure MeCN in the presence of a salt of organic cation provides the corresponding salts with the C_{60}^{2-} and C_{70}^{2-} dianions.[129] Advantages of this method include the relative stability of EtSNa in air and the selective reduction of fullerene to mono- or dianions even if the reducing agent is present in an excess.

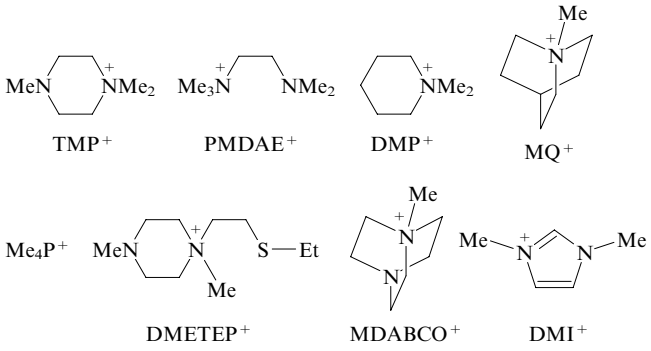


Figure 4. Organic cations (Ct^+) used in the synthesis of fullerene salts.

d. Multicomponent approach

Most of organic and organometallic donors (D) cannot reduce fullerenes and form molecular complexes with them. Complexes of this type have been prepared with metal porphyrins,[3, 130–133] metal dithiocarbamates,[134, 135] amines,[136, 137] aromatic hydrocarbons,[138, 139] substituted tetrathiafulvalenes [5, 37, 140, 141] and other compounds.[37, 141] These molecular complexes differ by the packing of fullerene molecules in the crystal;[37] complexes with close layered packing of fullerene molecules show interesting photophysical behaviour.[134, 142, 143] However, due to the neutral ground state, no magnetic spin ordering or conductivity occurs for these complexes.

The crystals of the molecular complexes $D\cdot C_{60}$ contain large cavities, which are usually occupied by solvent molecules. The size of the cavities is sufficient for accommodating small organic cations. When the cation is incorporated in the complex, fullerene will acquire a negative charge (−1, −2). Thus, the ionic complex is formed from three components not considering the solvent: $Ct^+DC_{60}^-$. The Ct component may be a strong donor that directly reduces the fullerene and determines its charge. Alternatively, similar ionic compounds of fullerene can be prepared by reducing fullerene by a different reducing agent in the presence of salts of Ct^+, *i.e.*, using cation metathesis. The second component (D) remains neutral and, due to the large size, determines the structure of the complex. By using various D components, ionic compounds with different crystal packing of fullerene anions can be prepared by this method, and by varying the size, the shape and the spin state of the Ct^+ cations, it is possible to affect the structure and the spin state of the whole complex.[144–148] An example of the multicomponent complex is $[\{Cr^I(C_6H_6)_2^{+\bullet}\}\{Co^{II}TPP(fullerene^-)\}C_6H_4Cl_2]$,† in which the strong donor $Cr(C_6H_6)_2$ (Ct component) reduces fullerene to the monoanion and $Co^{II}TPP$ is the neutral component determining the crystal structure.[148] Potentially, Ct and D can be represented by various cations (see Fig. 4) and neutral compounds (Fig. 5), respectively.

† Hereinafter, fullerene in the formulas stands for any fullerene (C_{60}, C_{70}, *etc.*) or a chemically modified derivative; $C_6H_4Cl_2$ is *o*-dichlorobenzene.

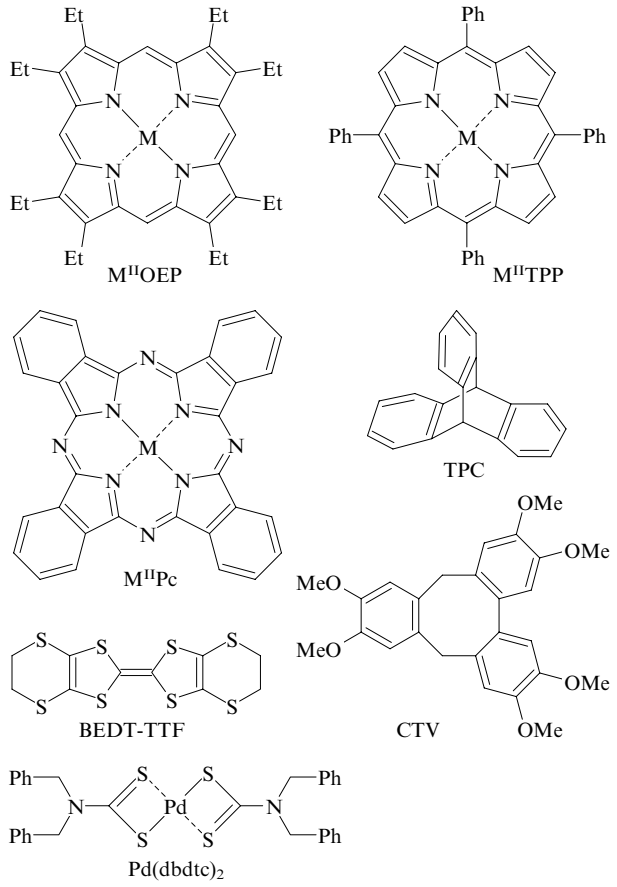


Figure 5. Neutral compounds (D) that were used to prepare multicomponent ionic fullerene complexes.

3. Preparation of crystals

Despite the diversity of the methods for generation of fullerene anions in solutions, only few methods exist for the preparation of single crystals of ionic compounds; therefore, many studies of ionic fullerene compounds were performed using powders, which precludes comprehensive investigations of the structures and properties of these products.

Single crystals of the salt $K_3C_{60}(THF)_{14}$ were prepared by slow cooling of a solution of C_{60} reduced by potassium in tetramethylethylenediamine containing THF and diethyl ether additives.[79] According to a modification of this method, a tube with a saturated solution of a fullerene salt is arranged at two different temperatures, the crystals being formed in the cold part of the solution.[80]

The crystals of the ferromagnetic TDAE·C_{60} complex were first obtained by an interdiffusion process; for this purpose, vessels with fullerene and TDAE solutions in toluene were connected by a solvent-filled bridge.[149,150] If the salt is poorly soluble in a polar solvent, it can be precipitated by diffusion of the corresponding cation. For example, diffusion of an acetonitrile solution of PPN^+Cl^- into a solution of the salt $\{Na^+(18\text{-crown-}6)\}_2C_{60}^{2-}(THF)_3$ in MeCN affords crystals of $(PPN^+)_2C_{60}^{2-}$, which is insoluble in MeCN.[151] The single crystals of ionic C_{60} compounds can also be prepared by slow diffusion of non-polar solvents (toluene, THF) into a solution of a fullerene salt in a polar solvent (DMF). This method is especially suitable for the preparation of salts with highly charged fulleride anions $(-2, -3)$.[74–76,152]

Initially, the electrochemical method was widely used to prepare ionic fullerene compounds. The $C_{60}^{-\bullet}$ and $C_{70}^{-\bullet}$ radical anions were generated by electrochemical reduction of fullerenes at a platinum cathode in an H-shaped cell for several days. As the supporting electrolytes, salts with bulky cations, Ph_4PX (X = Cl, Br, I),[66,67,153–155] Ph_4AsCl,[154,155] PPNCl[156,157] and $Ru(bipy)_3(PF_6)_2$, were used.[158] Either $C_6H_4Cl_2$ or mixtures of dichloromethane with toluene, chlorobenzene or THF served as solvents. The fullerene salts are poorly soluble in these solvents and crystallize on the cathode.

We developed a method for the preparation of crystals by diffusion of hexane into a solution containing an ionic compound Ct^+(fullerene$^{-\bullet}$) or a complex Ct^+D(fullerene$^{-\bullet}$). Slow diffusion (1–2 months) gives high-quality single crystals suitable for comprehensive investigation.[144–148]

IV. Structures and properties of ionic compounds of fullerenes

1. Magnetic properties of fullerene complexes with amines

The discovery of a ferromagnetic transition with the highest Curie temperature known among purely organic materials ($T_C = 16$ K) in the fullerene salt TDAE·C_{60} (**1**) arouse considerable interest in the ionic compounds of C_{60}.[11] Compounds of C_{60} with some other amines were prepared. It was asserted that some of them show ferromagnetism. More thorough studies indicated, however, that these products contain most likely a mixture of anions and amine adducts with fullerenes.[159–161] Thus, TDAE·C_{60} (Fig. 6*a*) is still the only one ferromagnetic compound of unsubstituted fullerene with amine whose properties were supported by numerous studies.

Several mechanisms of generation of the ferromagnetic state in TDAE·C_{60} are being debated.[164–166] It was shown by EPR that complete charge transfer from the donor to fullerene occurs in this salt; presumably, the ferromagnetism is related to the $C_{60}^{-\bullet}$ radical anions.[167] For the ferromagnetic state to arise in TDAE·C_{60}, the sample should be kept for several days at 20–100 °C (in a thermostat). Without this procedure, TDAE·C_{60} samples show only an antiferromagnetic behaviour.[168,169]

Rather recently, single crystals were prepared and the crystal structures were determined for antiferromagnetic[170] and 'thermostated' ferromagnetic phases.[162,166] The radical anions in both phases are packed into chains with short distances between the centres of the fullerene cages along the crystallographic axis *c* (see Fig. 6*a*). The fullerene radical anions are arranged in such a way that the six-membered ring of one fullerene is nearly parallel to a similar ring of another fullerene, and numerous C···C van der Waals contacts arise between them. It was found that the orientation of fullerenes relative to one another in the chains and the pattern of formation of C···C contacts between them differ for two phases, which is likely to be responsible for the difference in their magnetic properties.[166] Other differences between the phases were also noted; their influence on the magnetic properties is currently difficult to assess. In the ferromagnetic phase, the orientational ordering of the $C_{60}^{-\bullet}$ radical anions with a change in the crystal symmetry takes place at 170 K,

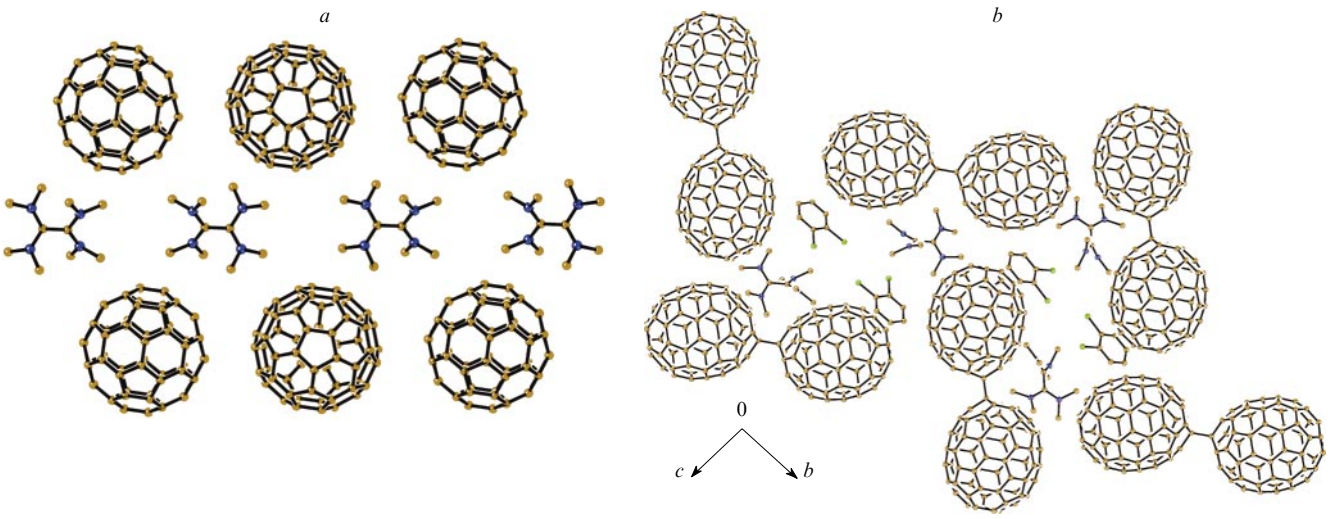


Figure 6. Crystal structure of the ferromagnetic complex TDAE·C_{60} (**1**) (two fullerene chains arranged along the direction *c* are shown) (*a*)[162] and projection of the $(TDAE^{+\bullet})C_6H_4Cl_2$ layers onto the hexagonal layer of $(C_{70}^{-})_2$ dimers in the complex $(TDAE^{+\bullet})(C_{70}^{-})(C_6H_4Cl_2)(n\text{-}C_6H_{14})_{0.5}$ (**2**) (hexane molecules are omitted) (*b*).[163]

whereas the symmetry of the antiferromagnetic phase remains the same as at room temperature. In the antiferromagnetic phase, all of the radical ions are equivalent down to very low temperatures, whereas in the ferromagnetic phase, two fullerene cages become symmetrically non-equivalent after transition to the ferromagnetic state. The reason is that at $T < T_C$, the $TDAE^{+\bullet}$ cations slightly shift along the *c* direction.[162]

No ferromagnetic behaviour was found in the TDAE compounds with higher fullerenes ($C_{70}-C_{96}$).[171,172] A possible reason is the difference between the electronic structures of the $C_{60}^{-\bullet}$ radical anion and the radical anions of higher fullerenes, because it was found that the negative charge in higher fullerene monoanions is delocalized over the whole surface rather than concentrated in the equatorial area as that in $C_{60}^{-\bullet}$ (Ref. 171). When analyzing this problem, one should take into account also the pronounced tendency of fulleride anions for dimerization. The compound TDAE·C_{60} is unique as the $C_{60}^{-\bullet}$ ions form there close-packed chains but no dimers are formed. This is apparently caused by the fact that the $TDAE^{+\bullet}$ cations sterically hinder the dimerization, preventing the $C_{60}^{-\bullet}$ radical anions from approaching each other for the formation of the C–C bond. Recently, it was shown that at a moderate pressure (7 kbar), the $C_{60}^{-\bullet}$ radical anions in TDAE·C_{60} still polymerize. The polymeric phase is retained after the pressure has been relieved, depolymerization being observed only on heating of the compound above 520 K. Polymerization induces transition of the compound from the ferromagnetic to the paramagnetic state. The polymeric phase is non-conducting, and its magnetic behaviour is described by the Curie law for a system with one spin per formula unit.[173,174]

Similarly to TDAE·C_{60}, complexes with C_{70}, namely, $(TDAE^{+\bullet})(C_{70}^{-})(C_6H_4Cl_2)(n\text{-}C_6H_{14})_{0.5}$ (**2**) and $(TDAE^{+\bullet}).(C_{70}^{-})(C_6H_4Cl_2)$ (**3**), have also ionic ground state, short contacts being present between the fullerenes; however, in the crystals of both complexes, the $C_{70}^{-\bullet}$ radical anions form dimers $(C_{70}^{-})_2$ linked by one C–C bond (Fig. 6*b*).[163] The formation of bulky diamagnetic dimers, $(C_{70}^{-})_2$, results in isolation of the $TDAE^{+\bullet}$ radical cations, and only paramagnetic behaviour being observed for the complexes. This is the main distinction of TDAE·C_{70} from TDAE·C_{60} in which both paramagnetic species ($C_{60}^{-\bullet}$ and $TDAE^{+\bullet}$) can be involved in the magnetic interaction. The dimeric state should be even more stable for the anions of C_{84}, C_{90} and C_{96} fullerenes than for C_{70}. Presumably, the paramagnetism of the TDAE complexes with higher fullerenes $C_{84}-C_{96}$ can also be caused by the formation of diamagnetic dimers $(C_n^{-})_2$ ($n = 84-96$).[172]

2. Complexes of fullerenes with metallocenes

Table 3 presents the compounds of C_{60} with metallocenes **4**–**16**. The donor properties of metallocenes vary over broad limits; therefore, they can form fullerene compounds characterized by different degrees of charge transfer (ranging from molecular complexes to ionic compounds with fullerene charge of −1 or −2). Upon coordination with fullerenes, the cyclopentadienyl rings of metallocenes are arranged parallel to the five-membered rings of fullerene [in $NiCp_2^*(C_{60})CS_2$ (**4**), the deviations are only 0.3°].[106] This coordination ensures the maximum overlap of the metallocene and fullerene π-orbitals and effective charge transfer.

The structures of fullerene compounds with metallocenes vary over a broad range and often depend on what solvent molecules are present in the structure. Metallocenes of moderate sizes [$Cr(C_6H_6)_2$, $Cr(PhMe)_2$ or $CoCp_2$] form close-packed three-dimensional structures, layers and zigzag chains (Fig. 7*a*). The packing of fullerenes with decamethylmetallocenes is quite diverse: isolated dianions in complex **16**, non-close-packed layers in complex **4** (Fig. 7*b*), zigzag chains in complex **10** (Fig. 7*c*).

The close packing of fullerene anions and the formation of short van der Waals contacts between them in ionic complexes with metallocenes favour the formation of σ-bonded fullerene structures. A linear polymer of C_{60}^{-} anions was found in the complex $\{Cr^{I}(PhMe)_2^{+}\}(C_{60}^{-})CS_2$ (**6**).[104] In this polymer, the C–C bond between the fullerenes is unusually long (2.12 Å) and the distance between the centres of the cages is also too long (9.6 Å). Due to the

Table 3. Ionic complexes of fullerenes with metallocenes.

Complex	Fullerene state	Structure and physical properties [a]	Ref.
$(NiCp_2^*)^+(C_{60}^{-\bullet})CS_2$ (**4**)	monomeric $C_{60}^{-\bullet}$	loosely packed layers, $r = 10.16$ Å, $\sigma = 10^{-2}$ S cm^{-1}	106
$(CoCp_2)^+(C_{60}^{-\bullet})CS_2$ (**5**)	monomeric $C_{60}^{-\bullet}$	zigzag chains, $r = 9.95$ Å, $N = 2$	102
$\{Cr^I(PhMe)_2^+\}(C_{60}^{-\bullet})CS_2$ (**6**)	polymerization is possible	linear polymer, $r = 9.60$ Å, $N = 2$	104
$\{Cr^I(PhMe)_2^{+\bullet}\}C_{60}^{-\bullet}$ (**7**)	dimerization	3D packing, $r = 10.01 - 10.28$ Å, $N = 6$, $2\,C_{60}^{-\bullet} \rightleftarrows (C_{60}^-)_2$ transition at 250 K	105, 175
$(Cr^IMes_2^{+\bullet})C_{60}^{-\bullet}$ (**8**)	dimerization is possible	3D packing, $N = 5$	176
$\{Cr^I(Ph_2)_2^{+\bullet}\}C_{60}^{-\bullet}$ (**9**)	dimerization at 100 K	tetragonal layers, $N = 4$	177
$(CrCp_2^*)^+C_{60}^{-\bullet}(C_6H_4Cl_2)_2$ (**10**)	dimerization	zigzag chains, $r = 10.01$ Å, $N = 2$, $2\,C_{60}^{-\bullet} \rightleftarrows (C_{60}^-)_2$ transition at 230 – 200 K, $\sigma = 6 \times 10^{-5}$ S cm^{-1}	100, 101
$\{Cr^I(C_6H_6)_2^{+\bullet}\}(C_{60}^{-\bullet})C_6H_4Cl_2$ (**11**)	"	3D packing, $r = 10.01 - 10.28$ Å, $N = 5$, $2\,C_{60}^{-\bullet} \rightleftarrows (C_{60}^-)_2$ transition at 240 – 160 K, $\sigma = 8 \times 10^{-4}$ S cm^{-1}	101, 178
$\{Cr^I(C_6H_6)_2^{+\bullet}\}(C_{60}^{-\bullet})PhCN$ (**12**)	"	$2\,C_{60}^{-\bullet} \rightleftarrows (C_{60}^-)_2$ transition at $T > 230$ K	101
$\{Cr^I(C_6H_6)_2^{+\bullet}\}_2(C_{70}^-)_2(C_6H_4Cl_2)_2$ (**13**)	"	$2\,C_{70}^{-\bullet} \rightleftarrows (C_{70}^-)_2$ transition at $T > 270$ K, $\sigma = 2 \times 10^{-5}$ S cm^{-1}	101
$(CoCp_2)^+)(C_{60}^{-\bullet})C_6H_4Cl_2$ (**14**)	"	$2\,C_{60}^{-\bullet} \rightleftarrows (C_{60}^-)_2$ transition at 260 – 340 K, $\sigma = 2 \times 10^{-2}$ S cm^{-1}	101
$(CoCp_2)_2^+(C_{70}^-)_2C_6H_4Cl_2$ (**15**)	"	$(C_{70}^-)_2$ dimer stable up to ~293 K	101
$(CoCp_2^*)_2^+(C_{60}^{2-})(C_6H_4Cl_2, PhCN)_2$ (**16**)	monomeric C_{60}^{2-} dianion	packing of isolated C_{60}^{2-} dianions, $r = 12.10$ Å	179, 180

[a] Here and in Tables 5 and 6, r is the minimum distance between the centres of fullerenes, N is the number of neighbouring fullerenes, σ is the electrical conductivity.

pronounced structural disorder, an attempt to correctly describe the structure of this polymer failed.[104] Perhaps, this polymer is a disordered phase containing dimers.

Dimerization of $C_{60}^{-\bullet}$ in compound **7** was assumed on the basis of X-ray powder diffraction data.[105, 175] The dimerization occurs at 250 K and is accompanied by a change in the g-factor of the EPR signal; simultaneously, the effective magnetic moment of the complex drops abruptly from 2.5 to 1.72 μ_B [*i.e.*, the system with two independent spins $S = 1/2$ transforms into a system with one spin $S = 1/2$ of $Cr^I(PhMe)_2^{+\bullet}$].[105] In complex **8**, no abrupt change in the magnetic properties takes place. However, at temperature < 170 K, the g-factor of the EPR signal smoothly shifts from 1.9925 [an intermediate value between the g-factors of EPR signals of $C_{60}^{-\bullet}$ and $(Cr^IMes_2)^{+\bullet}$] to $g = 1.9888$ at low temperature, which is inherent in isolated $(Cr^IMes_2)^{+\bullet}$. This

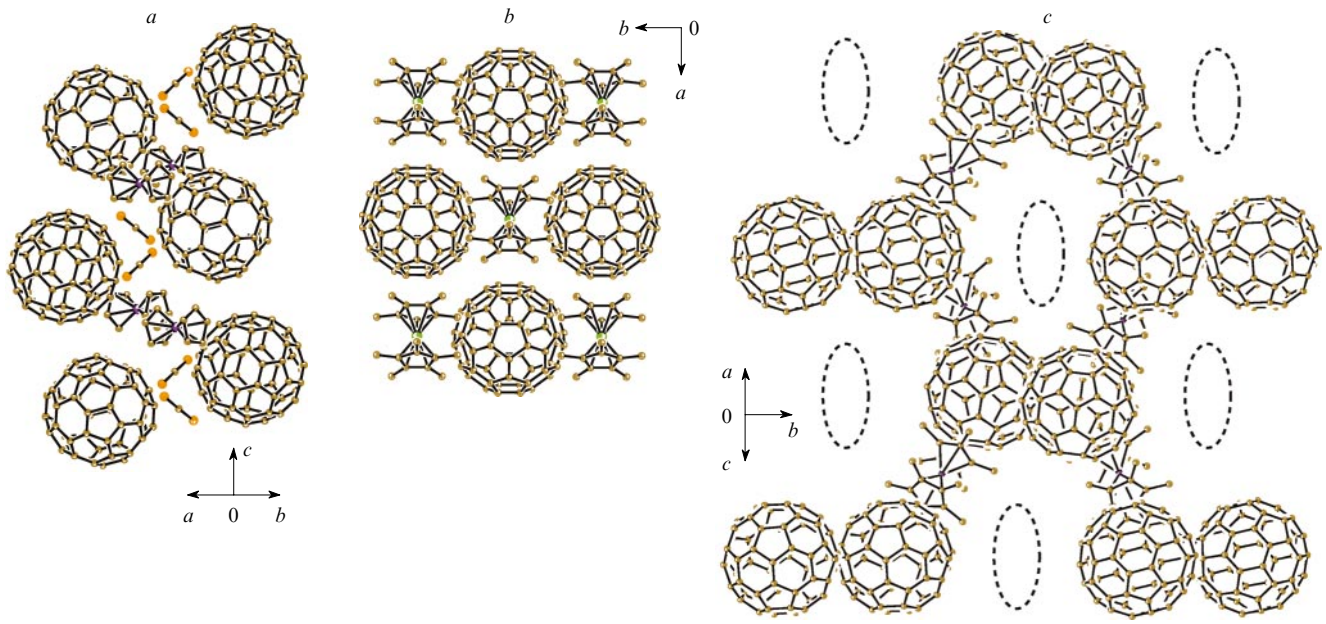


Figure 7. Zigzag fullerene chains in $(CoCp_2)^+(C_{60}^{-\bullet})CS_2$ (**5**) (*a*),[102] loose layers of the $C_{60}^{-\bullet}$ anions in $(NiCp_2^*)^+(C_{60}^{-\bullet})CS_2$ (**4**) (*b*),[104] projection of the crystal structure of $(CrCp_2^*)^+C_{60}^{-\bullet}(C_6H_4Cl_2)_2$ (**10**) along the [101] direction, *i.e.*, along the chain of the $(C_{60}^{-\bullet})_2$ dimers at 100 K (*c*).[100] The $C_6H_4Cl_2$ molecules form stacks, which are shown by dashed ellipses.

was also attributed to dimerization of $C_{60}^{-\bullet}$ but, unlike complex **7** where dimerization occurs as a first-order phase transition, dimerization is compound **8** is likely to be a second-order phase transition.[176]

We prepared a number of fullerene compounds with metallocenes as single crystals, which enabled the first study of the molecular structure of the $(C_{60}^{-})_2$ dimers.[100] Complex **10** at room temperature contains monomeric orientationally disordered $C_{60}^{-\bullet}$ radical anions. They form zigzag chains with short (10.11 Å) distances between the fullerene centres. The reversible transition related to dimerization occurs at 230–200 K. The monoclinic cell of the complex doubles in the dimeric phase along the direction *c*. At 200 K, the structure contains $(C_{60}^{-})_2$ dimers linked by one C–C bond. These dimers are statistically disordered between two states with different orientations, which transform into one another upon rotation of the dimer along the longer axis passing through the C–C bond between the carbon cages. As the temperature decreases, the occupancy of one of the two orientations increases, their ratio being 0.75 : 0.25 at 100 K. The dimer geometry was determined for the orientation with occupancy 0.75. The $(C_{60}^{-})_2$ dimers form chains along the [101] direction (see Fig. 7 *c*).

The effective magnetic moment of complex **10** is 4.20 μ_B at 300 K (Fig. 8 *a*), which is indicative of the presence of spins of $(CrCp_2^*)^+$ ($S = 3/2$) and $C_{60}^{-\bullet}$ ($S = 1/2$) (the calculated value for a system of two non-interacting spins $S = 3/2 + 1/2$ is 4.27 μ_B). The magnetic moment of compound **10** reversibly decreases to 3.85 μ_B at 230–200 K (see Fig. 8 *a*). Thus, at $T < 200$ K, diamagnetic $(C_{60}^{-})_2$ dimers are formed, and only the spins of $(CrCp_2^*)^+$ ($S = 3/2$) contribute to the magnetic moment of the complex (calculated value 3.87 μ_B).[100] At room temperature, complex **10** does not exhibit an EPR signal (Fig. 8 *b*) but at $T > 320$ K, a very broad signal appears with $g = 2.2210$ and half-width (ΔH) >100 mT. As the temperature increases, the signal narrows down to $\Delta H = 73$ mT (see Fig. 8 *b*). Apparently, instead of the two signals corresponding to $C_{60}^{-\bullet}$ and $(CrCp_2^*)^+$, due to the strong exchange interaction between these ions, one signal is observed with a *g*-factor intermediate between the *g*-factors characterizing the signals of $C_{60}^{-\bullet}$ and $(CrCp_2^*)^+$ (Ref. 181).

A new signal appears at $T < 230$ K, and its intensity substantially increases as the temperature decreases to 200 K. The signal is asymmetric, its principal component being at $g = 3.974$ ($\Delta H = 7$ mT) (see Fig. 8 *b*), and can be assigned to isolated $(CrCp_2^*)^+$ cations. It can be seen that dimerization destroys the magnetic exchange interaction between the $(CrCp_2^*)^+$ and $C_{60}^{-\bullet}$ ions observed in the phase that contains monomers and gives rise to magnetically isolated $(CrCp_2^*)^+$ cations in a dimer-containing phase. Indeed, the Weiss temperature (θ) for complex **10** is only −1 K in the 50–190 K range.[100]

Dimerization is also observed in complexes **11**–**15** (see Table 3). The $(C_{70}^{-})_2$ dimers linked by one C–C bond are more stable and start to dissociate at a nearly room temperature and above; therefore, unlike $(C_{60}^{-})_2$, they can be observed at room temperature.[101]

Decamethylcobaltocene is a strong donor and can form a compound with fullerene dianions, $(CoCp_2^*)_2^+(C_{60}^{2-}) \cdot (C_6H_4Cl_2,PhCN)_2$ (**16**). This compound was isolated as crystals, which made it possible to study the structure and the magnetic properties of the C_{60}^{2-} dianion.[179,180]

Complexes of fullerenes with metallocenes have a semiconductor-type conductivity with the values of 10^{-2}–10^{-5} S cm^{-1} at room temperature (see Table 3).

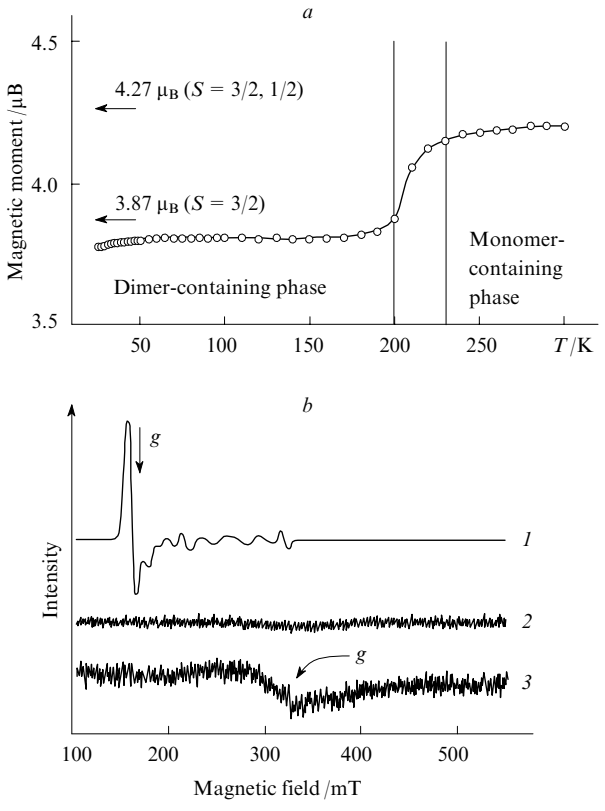


Figure 8. Temperature dependence of the effective magnetic moment of complex **10** (this behaviour is reversible) (*a*) and EPR spectra of complex **10** at 4 (*1*), 250 (*2*) and 410 K (*3*) (*b*).[100,181]

3. Fullerene salts with organic and organometallic cations

The first salts with $C_{60}^{-\bullet}$ and $C_{70}^{-\bullet}$ radical anions were obtained by electrocrystallization with bulky cations such as Ph_4P^+, PPN^+ and $Ru(bipy)_3^{2+}$. Currently, quite a few such salts are known (compounds **17**–**38**, Table 4). In these compounds, every fulleride anion is positioned in a highly symmetric cationic environment. The phenyl groups of the cations are located close to the six-membered rings of fullerene in such a way that these phenyl groups fully surround the $C_{60}^{-\bullet}$ anion. The conductivity of the salts with the Ph_4P^+ cation is only 10^{-4}–10^{-7} S cm^{-1} (Refs 66 and 182), which is obviously caused by large distances between the centres of the fullerene cages (~12.5 Å for all salts at a C_{60} van der Waals diameter of 10.18 Å).[66,153–155] The highest electrical conductivity was found for salts with the tris(bipyridine)ruthenium cation **28** (0.095 S cm^{-1}) and **30** (0.02 S cm^{-1}).[99] The conductivity in these salts is of the semiconductor type and is implemented by hopping. It was suggested [99] that the process may occur by charge transfer between the redox-active cations, $Ru(bipy)_3^+$ or $Ru(bipy)_3^{2+}$, and the anions, C_{60}^{2-} and $C_{60}^{-\bullet}$, respectively.

A number of salts with rather small organic cations (compounds **36**–**38**) were prepared. In structure **38**, $C_{60}^{-\bullet}$ form hexagonal close-packed layers,[116] the cations and

Table 4. Fullerene salts with organic and complex cations.

Cation	Compound	Charge	Preparation method	Ref.
Ph_4P^+	$(Ph_4P^+)_2(C_{60}^{-\bullet})Cl^-$ (**17**)	−1	electrocrystallization	153, 154
	$(Ph_4P^+)_3(C_{60}^{-\bullet})(Cl^-)_2$ (**18**)	−1	"	182
	$(Ph_4P^+)_2(C_{60}^{-\bullet})Br^-$ (**19**)	−1	"	154, 155
	$(Ph_4P^+)_2(C_{60}^{-\bullet})I^-$ (**20**) [a]	−1	"	66, 155
	$(Ph_4P^+)_2(C_{70}^{-\bullet})I^-$ (**21**)	−1	"	67
Ph_4As^+	$(Ph_4As^+)_2(C_{60}^{-\bullet})Cl^-$ (**22**)	−1	"	154, 155
PPN^+	$(PPN^+)(C_{60}^{-\bullet})PhCl$ (**23**)	−1	"	156, 157
	$(PPN^+)_2(C_{60}^{2-})$ (**24**)	−2	diffusion	70, 151
	$(PPN^+)(C_{60}^{-\bullet})(PhCN)THF$ (**25**)	−1	cation metathesis	73
	$(PPN^+)_2(C_{60}^{2-})(PPNCl)MeCN$ (**26**)	−2	the same	73
	$(PPN^+)_3(C_{60}^{3-})(MeCN)_2$ (**27**)	−3	"	73
$Ru(bipy)_3^{2+}$	$\{Ru^+(bipy)_3\}_2(C_{60}^{2-})(DMF)_6(C_6H_6)_2$ (**28**)	−2	diffusion	99
	$\{Ru^{2+}(bipy)_3\}(C_{60}^{-\bullet})_2$ (**29**)	−1	"	99
	$\{Ru^{2+}(bipy)_3\}(C_{60}^{-\bullet})_2$ (**29**)		electrocrystallization	158
	$\{Ru^{2+}(bipy)_3\}(C_{60}^{2-})(PhCN)_2(PhMe)_2$ (**30**)	−2	diffusion	99
$Co(dppe)^+$ (see [b])	$\{Co^+(dppe)_2\}(C_{60}^{-\bullet})(C_6H_4Cl_2)_2$ (**31**)	−1	reduction of a $Co(dppe)Br_2$ and C_{60} mixture with TDAE	183
$M^+(L)$ [c]	$\{K^+([2.2.2]cryptand)\}_2(C_{60}^{2-})(PhMe)_4$ (**32**)	−2	diffusion	76
	$\{Rb^+(benzo\text{-}18\text{-}crown\text{-}6)\}_3(C_{60}^{3-})(PhMe)(DMF)_{4.5}$ (**33**)	−3	"	75
	$\{K^+(18\text{-}crown\text{-}6)\}_3(C_{60}^{3-})(PhMe)_2$ (**34**)	−3	"	74
	$\{Na^+([2.2.2]cryptand)\}_4(C_{60}^{4-})$ (**35**)	−4	reduction of C_{60} with Na([2.2.2]cryptand)	72
$BnMe_3N^+$	$(BnMe_3N^+)_2(C_{60}^{2-})(NH_3)_3$ (**36**)	−2	diffusion in liquid NH_3	119
DMI^+	$(DMI^+)_3(C_{60}^{-\bullet})(I^-)_2$ (**37**)	−1	diffusion	127
TMA^+	$(Me_4N^+)(C_{60}^{-\bullet})(THF)_{1.5}$ (**38**)	−1	cation metathesis	116

[a] Initially [66] the salt composition was determined as $(Ph_4P^+)_2(C_{60}^{-\bullet})(I^-)_{0.35}$; later, it was shown [155] that in reality, all positions of iodide anions are occupied; [b] dppe is bis(diphenylphosphino)ethane; [c] L is macrocyclic ligand.

solvent molecules being located between the layers. Salt **38** has an electrical conductivity of 10^{-2} S cm^{-1} at room temperature and demonstrates the semiconducting behaviour with an activation energy of 0.36 eV. The measurements were carried out on pressed tablets; therefore, it was suggested that this behaviour may be caused by the presence of boundaries between the grains, and the real conductivity should be of the metallic type. High conductivity is attributable to the close packing of the fulleride anions in the crystal. A decrease in the magnetic susceptibility for compound **38** occurs below 200 K.[116] This may be caused by dimerization of $C_{60}^{-\bullet}$, which usually occurs in close-packed ionic compounds of C_{60} in the range of 130–280 K.[100, 101, 105, 178]

A salt with *N*,*N*′-dimethylimidazolium cations, $(DMI^+)_3(C_{60}^{-\bullet})(I^-)_2$ (**37**), was prepared;[27] it has a unique structure with a three-dimensional network of DMI^+ and I^- ions, which accommodates the $C_{60}^{-\bullet}$ radical anions. The network is composed of $(DMI^+)_3(I^-)$ aggregates in which DMI^+ and I^- are combined by $H(DMI^+)\cdots(I^-)$ hydrogen bonds. The arrangement of the $C_{60}^{-\bullet}$ radical anions can be roughly described as a three-dimensional hexagonal packing composed of loose hexagonal layers of fulleride anions (the distance between the centres is 13.36 Å). In this packing, the number of nearest neighbours is only 6 (the distance between the centres is 11.05 Å); they are located in adjacent layers and form a trigonal prism around the central anion (Fig. 9). The relatively long distances between $C_{60}^{-\bullet}$ prevent them from dimerization. The spin coupling in the complex is antiferromagnetic, the Weiss temperature is −9.6 K in the 80–300 K range. Compounds **37** exhibits a broad EPR signal due to $C_{60}^{-\bullet}$ (21.5–23.1 mT) in the range of 82–297 K with rather large *g*-factor (2.0035 at 297 K). The signal sharply narrows down below at 82 K due to a structural transition or sharp freezing of the rotation of $C_{60}^{-\bullet}$.[127]

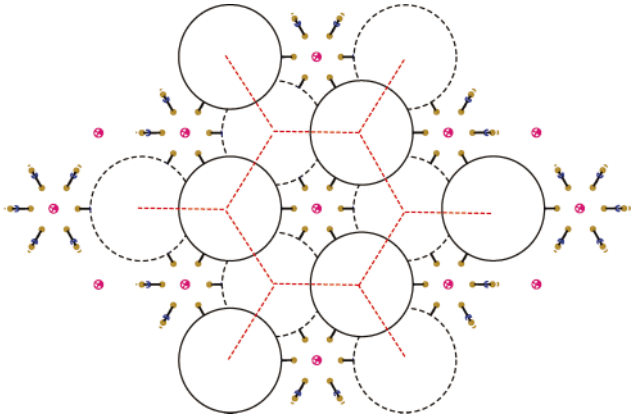


Figure 9. Formation of the three-dimensional hexagonal fullerene structure in compound **37**.[127]
The view along the [001] direction and chains of aggregated $(DMI^+)_3(I^-)$ ions are shown. The disordered $C_{60}^{-\bullet}$ ions of two layers are shown by solid and dashed circles, respectively, and dashed lines show the shortest distances (11.05 Å) between their centres.

4. Fullerene salts with metal porphyrins. Coordination of fullerene anions to cobalt(II) porphyrins

Due to strong redox properties some metal porphyrins can be used for the reduction of fullerenes. However, crystalline products were not isolated, and therefore it was impossible to study the structure of the ionic compounds formed. For example, chromium(II) tetraphenylporphyrin ($Cr^{II}TPP$) reduces fullerene in THF to give the salts ($Cr^{III}TPP^{+}$). $.C_{60}^{-\bullet}(THF)_3$ (**39**) (Table 5).[68] The reaction is reversible; upon the addition of toluene, the equilibrium shifts toward neutral C_{60}. In pure toluene, the reduction of C_{60} does not occur. Compound **39** is paramagnetic and has the effective magnetic moment $\mu_{ef} = 4.2\ \mu_B$, which is characteristic of a system of two non-interacting spins [$S = 3/2$ due to $Cr^{III}(TPP)^{+}$ and $S = 1/2$ due to $C_{60}^{-\bullet}$].

Tetra-*p*-tolylporphyrintin(II) ($Sn^{II}TpTP$) ($E_{ox} = -1.17$ V) reacts with C_{60} in the presence of MeIm to give the salt $(Sn^{IV}TpTP)(MeIm)_2(C_{60}^{-\bullet})_2$ (**40**). *N*-Methylimidazole stabilizes the $Sn^{IV}TpTP^{2+}$ cation and, hence, the whole complex.[63]

Table 5 presents also a number of ionic fullerene compounds with cobalt(II), zinc and manganese(II) porphyrins (compounds **41**–**56**).

As opposed to strong donors, $Cr^{II}TPP$ and $Sn^{II}TpTP$, most of metal porphyrins cannot reduce fullerenes C_{60} and C_{70} and form neutral complexes with them.[3, 130–132, 133, 148, 192] Despite the absence of charge transfer, weak metal–carbon(fullerene) binding is observed in the complexes with cobalt(II) octaethyl- and tetraphenylporphyrins, iron(III) tetraphenylporphyrin and iron(II) octaethylporphyrin. The length of the M···C(C_{60}) contacts is 2.57–2.69 Å.[1, 133, 148, 186, 192] These contacts are shorter than the sum of the van der Waals radii of M and C (> 3.1 Å) but considerably longer than the Co–C bond in alkylcobalamines (1.99–2.03 Å).[193] Much stronger binding of $Co^{II}TPP$ was found in compounds with fullerene anions. For example, in the ionic complexes $[\{Cr^{I}(C_6H_6)_2^{+\bullet}\}.\{Co^{II}TPP(fullerene^{-})\}C_6H_4Cl_2]$ with C_{60} and $C_{60}(CN)_2$, the length of Co···C(fullerene^{-}) coordination bonds is 2.28–2.32 Å. The coordination is of the σ-type (Fig. 10). The coordinated $\{Co^{II}TPP(fullerene^{-})\}$ anions are diamagnetic.[148, 184, 185] It is of interest that only cobalt(II) porphyrin complexes form stable coordination bonds with fullerene anions, while other metal porphyrins (M = Fe^{II}, Mn^{II}, Zn^{II}, Cu^{II}) seem not to form such bonds.

The σ-$\{Co^{II}TPP\cdot(C_{60}^{-})\}$ coordination anions are fairly stable and start to dissociate only above 320 K (in compound **43**),[185] *i.e.*, they are more stable than the corresponding dimers, $(C_{60}^{-})_2$ linked by one C–C bond (dissociation of these dimers starts at 130–280 K).[100, 101, 105, 178]

In some cases, the Co–C(C_{60}^{-}) bonds may be destabilized. Changes in the Co–C_{60}^{-} binding are detected using EPR data and SQUID measurements, as dissociation of the Co–C bond produces two paramagnetic species [cobalt(II)

Table 5. Ionic fullerene compounds with metal porphyrins.

Metal porphyrin	Compound	Fullerene charge	Type of fullerene structure and properties	Ref.
$Cr^{II}TPP$	$(Cr^{III}TPP^{+})C_{60}^{-\bullet}(THF)_3$ (**39**)	−1	monomeric $C_{60}^{-\bullet}$	68
$Sn^{II}TpTP$	$(Sn^{IV}TpTP^{2+})(MeIm)_2(C_{60}^{-\bullet})_2$ (**40**)	−1	the same	63
$Co^{II}TPP$	$\{Cr^{I}(C_6H_6)_2^{+\bullet}\}_{1.7}[\{Co^{II}TPP(C_{60})\}_2^{1.7-}](C_6H_4Cl_2)_{3.3}$ (**41**)	−0.85	σ-$\{Co^{II}TPP(C_{60}^{-})\}$	148
	$\{Cr^{I}(C_6H_6)_2^{+\bullet}\}_2[Co^{II}TPP\{C_{60}(CN)_2^{-}\}]\{C_{60}(CN)_2^{-\bullet}\}(C_6H_4Cl_2)_3$ (**42**)	−1	σ-$[Co^{II}TPP\{C_{60}(CN)_2^{-}\}]$	148, 184
	$\{Na^{+}([2.2.2]cryptand)\}\{Co^{II}TPP\cdot(C_{60}^{-})\}(C_6H_4Cl_2)_2$ (**43**)	−1	σ-$\{Co^{II}TPP(C_{60}^{-})\}$, dissociates at $T > 320$ K	185
$Co^{II}OEP$	$(Me_4P^{+})\{Co^{II}OEP(C_{60}^{-})\}(PhCN)_{0.75}(C_6H_4Cl_2)_{0.25}$ (**44**)	−1	σ-$\{Co^{II}OEP(C_{60}^{-})\}$	126
	$(MQ^{+})\{Co^{II}OEP(C_{60}^{-})\}C_6H_4Cl_2$ (**45**)	−1	σ-$\{Co^{II}OEP(C_{60}^{-})\}$	186
	$\{(MDABCO^{+})Co^{II}OEP(C_{60}^{-})\}(PhCN)_{0.67}(C_6H_4Cl_2)_{0.33}$ (**46**)	−1	σ-$\{(MDABCO^{+})Co^{II}OEP(C_{60}^{-})\}$, reversible dissociation of the Co–C(C_{60}^{-}) bond in the range 50–250 K	126
$Co^{II}TPP$	$\{(Cs^{+})Co^{II}TPP(C_{60}^{-\bullet})\}(PhCN)_{1.64}(C_6H_4Cl_2)_{0.36}MeCN$ (**47**)	−1	non-bonded $Co^{II}TPP$ and $C_{60}^{-\bullet}$	187
ZnTPP	$\{(TMP^{+})_2ZnTPP\}(C_{60}^{-})_2(PhCN)C_6H_4Cl_2$ (**48**)	−1	dimerization $2\,C_{60}^{-\bullet} \rightleftarrows (C_{60}^{-})_2$ at 210–160 K	128
$Mn^{II}TPP$	$\{(TMP^{+})_2Mn^{II}TPP\}(C_{60}^{-})_2(PhCN)C_6H_4Cl_2$ (**49**)	−1	dimerization $2\,C_{60}^{-\bullet} \rightleftarrows (C_{60}^{-})_2$ at 200–160 K	128
$Co^{II}TMPP$	$\{(MDABCO^{+})Co^{II}TMPP\}_2(C_{60}^{-})_2(PhCN)_{1.5}(C_6H_4Cl_2)_{2.5}$ (**50**)	−1	isolated $(C_{60}^{-})_2$, dimers linked by two C–C bonds	188, 189
ZnTMPP	$\{(MDABCO^{+})ZnTMPP\}_2(C_{60}^{-})_2(PhCN)_{1.85}(C_6H_4Cl_2)_{2.15}$ (**51**)	−1	the same	190
$Co^{II}TPP$	$\{(MDABCO^{+})_2Co^{II}TPP\}(C_{60}^{-\bullet})_2(PhCN)_{1.6}(C_6H_4Cl_2)_{4.4}$ (**52**)	−1	monomeric $C_{60}^{-\bullet}$, chains, $r = 10.34$ Å, $N = 2$	191
$Mn^{II}TPP$	$\{(MDABCO^{+})_2Mn^{II}TPP\}(C_{60}^{-\bullet})_2(PhCN)_{1.8}(C_6H_4Cl_2)_{4.2}$ (**53**)	−1	monomeric $C_{60}^{-\bullet}$, chains, $r = 10.43$ Å, $N = 2$, $\theta = -2$ K	191
ZnOEP	$\{(MDABCO^{+})ZnOEP\}C_{60}^{-\bullet}(PhCN)_{0.75}(C_6H_4Cl_2)_{0.25}$ (**54**)	−1	monomeric $C_{60}^{-\bullet}$, chains, $r = 10.56$ Å, $N = 2$, $\theta = -18$ K	186
$Mn^{II}OEP$	$\{(MDABCO^{+})Mn^{II}OEP\}C_{60}^{-\bullet}(PhCN)_{0.88}(C_6H_4Cl_2)_{0.12}$ (**55**)	−1	monomeric $C_{60}^{-\bullet}$, chains, $r = 10.70$ Å, $N = 2$, $\theta = -2.5$ K	186
$Mn^{II}TPP$	$\{(MDABCO^{+})_2Mn^{II}TPP\}C_{60}^{2-}(C_6H_4Cl_2)_4(MeCN)_2$ (**56**)	−2	isolated C_{60}^{2-} dianions	129

Note. TMPP is tetrakis(4-methoxyphenyl)porphyrin.

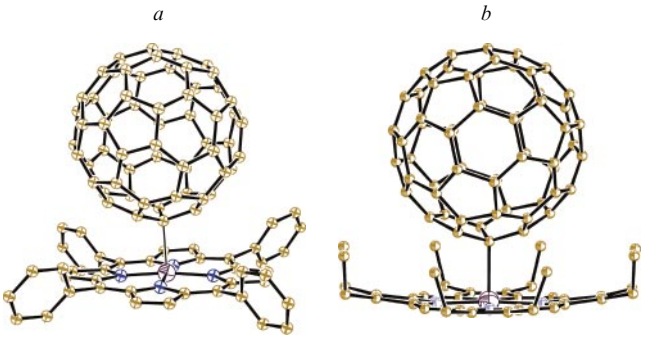


Figure 10. Molecular structures of the coordination anions: σ-{$Co^{II}TPP(C_{60}^{-})$} in complex **43** (*a*),[185] σ-{$(Co^{II}OEP(C_{60}^{-})$} in complex **45** (*b*).[186]

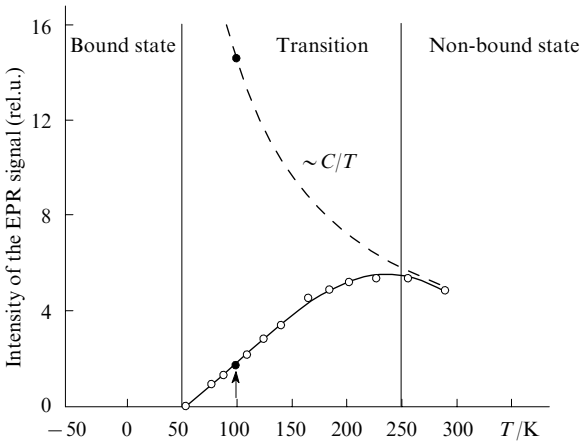


Figure 11. Temperature dependence of the integrated intensity of the EPR signal for complex **46**.[126]
The dashed line shows the expected integrated intensity of the EPR signal for a system of two non-interacting spins $S = 1/2$ (C is the Curie constant).

porphyrin and $C_{60}^{-\bullet}$ radical anion] and the compound passes from the diamagnetic to paramagnetic state. Complexes with such transitions are of interest for the design of molecular switches, as they provide reversible change of magnetic, conductive and optical properties.

The nitrogen-containing $MDABCO^+$ cation (see Fig. 4) and C_{60}^- anion bind to $Co^{II}OEP$ to give the complex [$(MDABCO^+)Co^{II}OEP(C_{60}^-)$] (**46**) with six-coordinate cobalt.[126] The complex is diamagnetic and does not produce EPR signals at low temperatures (4–50 K) (Fig. 11), which is indicative of the existence of the $Co-C(C_{60}^-)$ bond. A new broad signal ($g = 2.1188$, $\Delta H = 52.0$ mT at room temperature) appears at $T > 50$ K, and its intensity increases with temperature (see Fig. 11). This signal appears due to dissociation of the Co–C bonds to give two paramagnetic species, $(MDABCO^+)Co^{II}OEP$ and $C_{60}^{-\bullet}$, which produce only one EPR signal due to magnetic exchange interaction between them. The integrated intensity of the signal at $T > 250$ K indicates that all diamagnetic species have dissociated to give paramagnetic species (see Fig. 11). The Co–C bond dissociation occurs over a broad temperature range (~200 K) and does not induce a phase transition, which usually accompanies dissociation of the $(C_{60}^-)_2$ dimers linked by one C–C bond. Among the dimeric structures, the dissociation of $(C_{60}^-)_2$ is not accompanied by a first-order phase transition only in the complex $(Cr^{I}Mes_2)C_{60}$ (**8**).[176] The length of the $Co-C(C_{60}^-)$ coordination bond in compound **46** is 2.51 Å at 100 K (see the arrow in Fig. 11). This is much greater than the length of analogous bonds in stable coordination anions {Co^{II}(porphyrin)(fullerene$^-$)} (2.26–2.32 Å).[126, 148, 184, 185] Since the structure of complex **46** was solved at 100 K and the Co–C bonds already start to dissociate at $T > 50$ K, the distance of 2.51 Å should be intermediate between the bonded and non-bonded states of the $Co^{II}OEP$ and C_{60}^- pair.[126]

The $Co-C(C_{60}^-)$ bonds are formed most likely by electrons of the LUMO‡ of C_{60}^- and the d_{z^2} orbital of cobalt(II) porphyrin. Neutral fullerenes having no electrons in the LUMO do not form such bonds. The electrons involved in the coordination bond are paired; therefore, the {Co^{II}(porphyrin)(fullerene$^-$)} anions are diamagnetic. Optical spectroscopy data indicate that upon coordination, the negative charge is concentrated on the fullerene sphere. The fullerene anions with one electron in the LUMO (π^{*1}) can be considered as single-electron ligands similar to NO, which also has one electron in the π*-orbital. The coordination structure of $Co^{II}TPP(NO)$ has a similar electron configuration with {$Co^{II}TPP(C_{60}^-)$} and is also diamagnetic.[194]

No coordination of $C_{60}^{-\bullet}$ to $Co^{II}TPP$ is present in complex **47**. Perhaps, the bulky $Cs^+(PhCN)_{1.64}MeCN$ cations prevent $C_{60}^{-\bullet}$ and $Co^{II}TPP$ from approaching each other. As a result, the $Co-C(C_{60}^{-\bullet})$ distances are rather long (2.55–3.07 Å), and the complex exhibits two EPR signals, one due to $Co^{II}TPP$ and one due to $C_{60}^{-\bullet}$ (Ref. 187).

Neutral metal porphyrin molecules can be inserted into the ionic complexes $Ct^+(C_{60}^{-\bullet})$ by means of coordination bonding to nitrogen-containing cations such as TMP^+, $PMDAE^+$ and $MDABCO^+$ (see Fig. 4). This can be done using metal porphyrins (M = Zn, Co^{II}, Mn^{II}, Fe^{II}) capable of axial coordination. Positively charged structures $(Ct^+)_n${M^{II}(porphyrin)} ($n = 1$ or 2) formed in solution co-crystallize with fullerene mono- or dianions as the complexes {$(Ct^+)_xM^{II}$(porphyrin)}$(C_{60}^{n-})_y$ ($n = 1$ or 2, $x = ny$) (see Table 5). Metal tetraphenylporphyrins complexed with fullerenes form structures in which two cations are coordinated to the metal atom: {$(MDABCO^+)_2M^{II}TPP$} [M = Co (for compound **52**), Mn (for compound **53**), Fig. 12 *a*].[191] These complexes comprise zigzag chains of $C_{60}^{-\bullet}$ radical anions whose spins interact antiferromagnetically (Weiss temperature varies from −2 to −13 K). Complex **56** containing {$(MDABCO^+)_2Mn^{II}TPP$} and C_{60}^{2-} dianions was also prepared.[129]

Metal tetra(4-methoxyphenyl)porphyrins coordinate only one cation to give $(MDABCO^+)M^{II}TMPP$ [M = Co^{II} (for compound **50**), Zn (for compound **51**), see Fig. 12 *b*].[183–185] In these complexes, unusual paramagnetic dimers, $(C_{60}^-)_2$, connected by two C–C bonds appear (their properties are described in Section V.2). Metal(II) octaethylporphyrins complexed with fullerenes also coordinate only one cation: $(MDABCO^+)M^{II}OEP$ [M = Zn (for compound **54**), Mn (for compound **55**), Fig. 12 *c*] and fullerenes

‡ Hereinafter, the LUMO and the HOMO stand for the lowest unoccupied and higher occupied molecular orbitals of neutral fullerene.

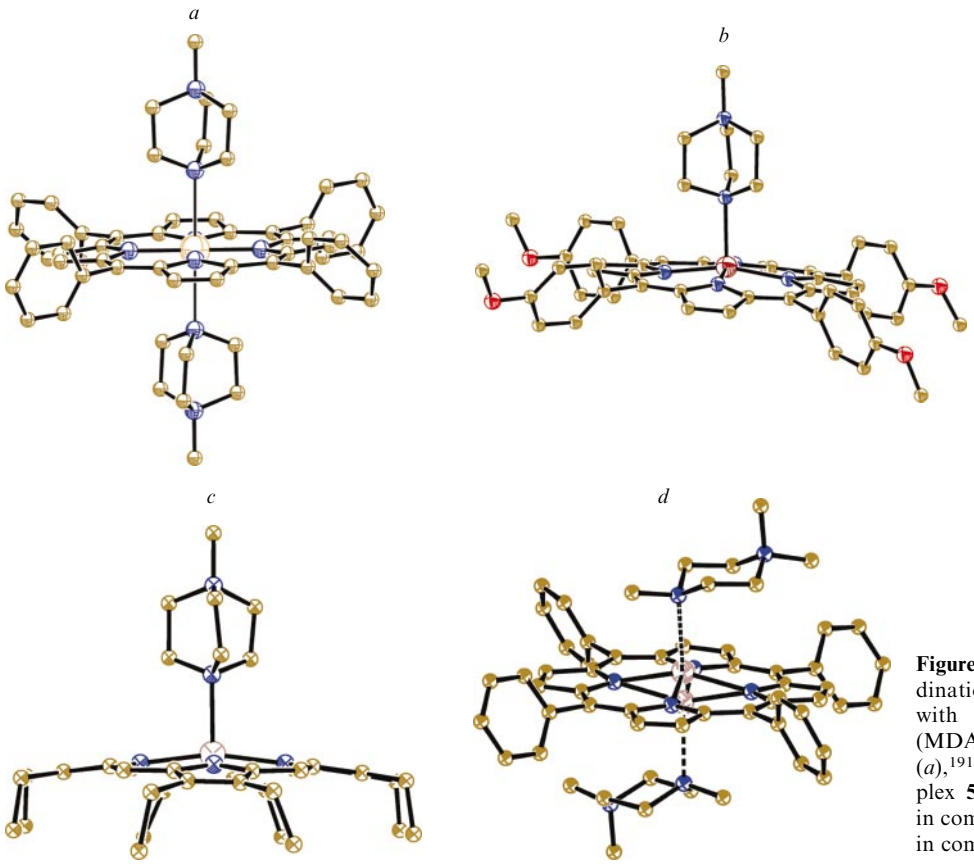


Figure 12. Positively charged coordination structures of metal porphyrins with nitrogen-containing cations $(MDABCO^+)_2Co^{II}TPP$ in complex **52** (*a*),[191] $(MDABCO^+)ZnTMPP$ in complex **51** (*b*),[190] $(MDABCO^+)Mn^{II}OEP$ in complex **55** (*c*),[186] $(TMP^+)_2Mn^{II}TPP$ in complex **49** (*d*).[121]

are located on the opposite side of the porphyrin macrocycle without coordination.[186] The absence of coordination can be attributed to the fact that $MDABCO^+$ is a more potent ligand than $C_{60}^{-\bullet}$, and upon its coordination the metal atom deviates from the porphyrin plane towards the $MDABCO^+$ nitrogen atom, which destabilizes the bond between the metal and $C_{60}^{-\bullet}$. In structures **54** and **55**, monomeric $C_{60}^{-\bullet}$ are packed in zigzag chains (Fig. 13) in which the spins undergo antiferromagnetic interaction with $\theta = -2.5$ and -18 K, respectively.[186]

The TMP^+ cation (see Fig. 4), like $MDABCO^+$, is also coordinated to metal porphyrins, and were used to prepare ionic complexes **48** and **49** (see Table 5). Out of the two cations that surround the metal atom in $(TMP^+)_2M^{II}TPP$ (M = Zn, Mn, Fig. 12*d*), only one is coordinated. Thus, the metals in porphyrins are five-coordinate. Complexes **48** and

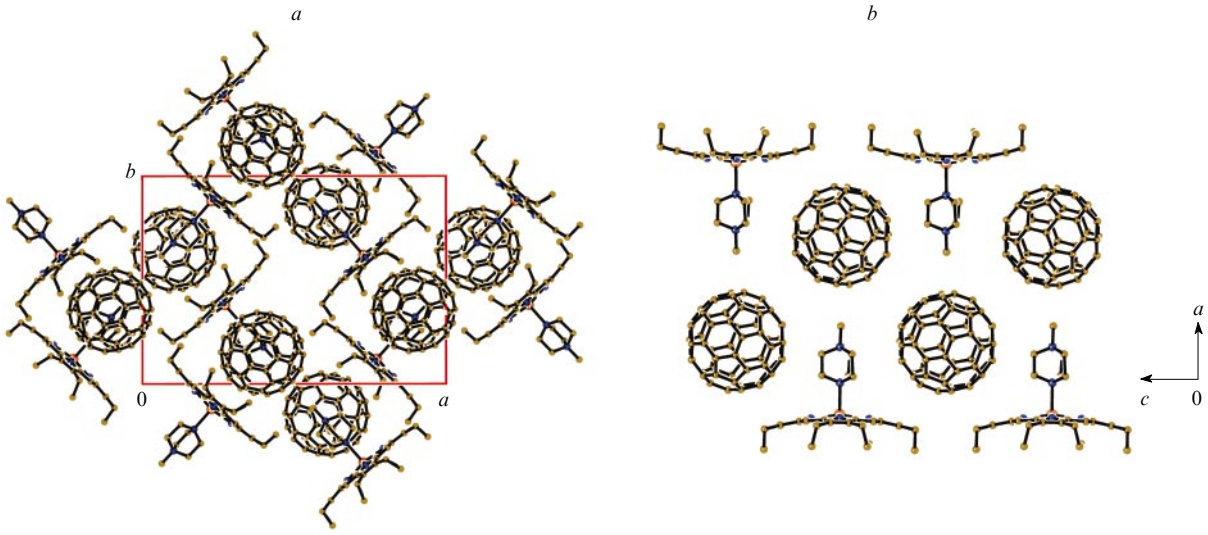


Figure 13. View of the crystal structure of complex **54** along the [001] direction (*a*), view of zigzag fullerene chains along the [010] direction (*b*).[186] The solvent molecules are not shown.

49 have layered structures. The fullerene layers are composed of the $C_{60}^{-\bullet}$ dimers, which are formed at 210–150 K. Dimerization induces transition of compound **48** from the paramagnetic to diamagnetic state and a decrease in the magnetic moment of compound **49**.[128]

5. Ionic compounds with metal phthalocyanines

Metal phthalocyanines (MPc) constitute one more class of macrocyclic compounds that can participate in the formation of ionic complexes with fullerenes. The synthesis was performed by the method used previously to prepare ionic complexes of fullerenes with metal porphyrins. However, the fullerene complexes with phthalocyanines are formed by a different pattern. Metal phthalocyanines coordinate anionic ligands (EtS^- and I^-) present in the solution, and, consequently, the complex contains two different anions: $M^{II}Pc(An^-)$ and $C_{60}^{-\bullet}$. This procedure was used to prepare $[Mn^{II}Pc(EtS^-)_x(I^-)_{1-x}](C_{60}^{-\bullet})(PMDAE^+)_2C_6H_4Cl_2$ (x = 0.87) (**57**) and $[Zn^{II}Pc(EtS^-)_y(I^-)_{1-y}]_2(C_{60}^-)_2(PMDAE^+)_4 .C_6H_4Cl_2$ (y = 0.5) (**58**) (for the formula of $PMDAE^+$, see Fig. 4).[195]

Compounds **57** and **58** have layered structure. Honeycomb-like (hexagonal) fullerene layers with three neighbours at every $C_{60}^{-\bullet}$ anion contain large voids occupied by solvent molecules. These layers alternate with layers containing $M^{II}Pc(An^-)$ (Fig. 14). In complex **57**, the distances between the fulleride anions are sufficiently large to prevent them from dimerization, whereas the presence of short $C_{60}^{-\bullet}\cdots C_{60}^{-\bullet}$ contacts in structure **58** induces dimerization. Negatively charged fullerene and phthalocyanine layers are held together by the $PMDAE^+$ cations located between the layers. The packing of the spherical fullerene anions and planar phthalocyanine anions is achieved by fullerenes being arranged between the phenylene groups of phthalocyanines (see Fig. 14). However, no strong $\pi-\pi$ interaction, typical of the ionic complexes of fullerenes with metal porphyrins, is observed in fullerene–phthalocyanine complexes.

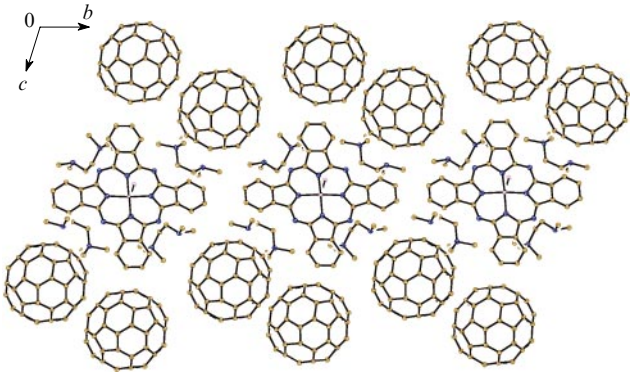


Figure 14. View along the fullerene and phthalocyanine layers in the structure of complex **57**.[195]

6. Fullerene salts with metal cations

An extensive series of compounds of metal cations with the C_{60}^{2-} dianions (**59**–**64**) were prepared as crystals in liquid ammonia.[117–118, 120–121] All of the salts were structurally characterized; for all compounds, the formation of linear chains with rather short distances between the centres of fullerene anions was demonstrated (9.88–10.05 Å) (Table 6). However, at room temperature, the crystals are unstable and decompose by losing ammonia from the crystal lattice. By a similar reaction with C_{70}, salts **65**–**67** consisting of zigzag polymers, $(C_{70}^{2-})_n$ and $(C_{70}^{3-})_n$, were prepared for the first time.[122–124]

In structure **68**, the $C_{60}^{-\bullet}$ radical anions are packed in chains (Fig. 15 *a*) with a short (9.86 Å) distance between the cage centres, giving rise to numerous van der Waals C···C contacts between them.[73] Five THF molecules are coordinated around each K^+ cation, whereas the sixths coordination site is vacant for close approach of a fullerene anion, and short K···C contacts (3.21–3.36 Å) with the $C_{60}^{-\bullet}$ [6,6]-bond are formed. Dimerization is apparently sterically hindered by the bulky $K^+(THF)_5$ cations.[80]

As regards the motif of the C_{60}^{3-} anions, structure **69** resembles the structure of M_3C_{60} superconductors with face-centred cubic (fcc) lattice, but the distances between the C_{60}^{3-} anions are much longer than in M_3C_{60}, and the compound does not show a metallic behaviour.[79] One of the three K^+ cations is proximate to the five-membered C_{60} ring being a bridge between two fullerene anions. Two other K^+ cations are located above and below the C_{60}^{3-} anion and form contacts with six-membered rings of C_{60} (Fig. 15 *b*). The other coordination sites around the K^+ cation are occupied by THF molecules.[79]

A series of fullerene compounds with alkali metals, $M_n^+(C_{60}^{n-})(THF)_y$ (n = 1–3), were obtained;[77, 78, 81, 82] however, they were not characterized adequately for discussing their structures or physical properties. The magnetic properties were studied for $Na^+(C_{60}^-)(THF)_5$ (**70**): at room temperature, μ_{ef} = 1.7 μ_B, which attests to a system containing one spin $S = 1/2$ per formula unit. The phase containing monomers shows a strong antiferromagnetic spin coupling with $\theta = -56$ K. The abrupt decrease in the magnetic moment observed at 200 K may be attributed to dimerization.[81] The compound $K_3C_{60}(THF)_7$ (**71**) was used to prepare the superconducting phase K_3C_{60}. Tetrahydrofuran is removed from the salt by evacuation and then the salt is maintained at 300 °C for 12 h. During cooling down, heat evolution is observed in the sample at 103 °C; this is attributed to transition to a more stable K_3C_{60} phase with a fcc lattice. The sample becomes superconducting, the content of the superconducting phase being 31%.[82]

The compound $(Na^+)_x(THF)_yC_{60}^-$ ($x \approx 0.4$, $y \approx 2.2$) (**72**) has a conductivity of 50 S cm^{-1} at room temperature. As the temperature decreases, the conductivity increases to reach 1000 S cm^{-1} at 100 K, indicating the metallic behaviour.[77, 78] The crystal cell of the compound is presumably hexagonal with the small parameter a = 9.965 Å. This corresponds to close packing of fullerenes in the hexagonal layer.[84] Thus, high conductivity of compound **72** can be explained by partial charge transfer ($\delta = 0.4$) and the formation of close-packed fullerene layers. At 170 K, a phase transition accompanied by a slight decrease in the unit cell parameters takes place in structure **72**, resulting in the transformation of the compound from the metal to the dielectric.[84, 85] Unfortunately, the absence of X-ray diffraction data (except for the cell parameters) precludes understanding of the nature of this transition. Analogous compounds were obtained with the K^+ and Li^+ cations. Compound **73** with the Li^+ cation also has a rather high conductivity (30 S cm^{-1} at room temperature) but the temperature dependence of the conductivity is of the semi-

Table 6. Compounds of fullerenes C_{60} and C_{70} with metal cations.

Complex [a]	State	Structure, physical properties	Ref.
$\{Cd^{2+}(NH_3)_6\}(C_{60}^{2-})(NH_3)_3$ (**59**)	monomeric C_{60}^{2-}	linear chains, $r = 9.97$ Å, $N = 2$	117
$\{Mn^{2+}(NH_3)_6\}(C_{60}^{2-})(NH_3)_3$ (**60**)	the same	linear chains, $r = 9.99$ Å, $N = 2$	117
$\{Co^{2+}(NH_3)_6\}(C_{60}^{2-})(NH_3)_3$ (**61**)	"	linear chains, $r = 9.89$ Å, $N = 2$	120
$\{Zn^{2+}(NH_3)_6\}(C_{60}^{2-})(NH_3)_3$ (**62**)	"	linear chains, $r = 10.01$ Å, $N = 2$	120
$\{Ni^{2+}(NH_3)_6\}(C_{60}^{2-})(NH_3)_3$ (**63**)	"	linear chains, $r = 9.88$ Å, $N = 2$	118
$\{Ba^{2+}(NH_3)_7\}(C_{60}^{2-})NH_3$ (**64**)	"	linear chains, $r = 10.05$ Å, $N = 2$	121
$\{Ba^{2+}(NH_3)_7\}(C_{70}^{2-})(NH_3)_9$ (**65**)	polymer C_{70}^{2-}	–	122
$\{Sr^{2+}(NH_3)_8\}(C_{70}^{2-})(NH_3)_3$ (**66**)	the same	–	122, 123
$\{Sr^{2+}(NH_3)_8\}_3(C_{70}^{3-})_2(NH_3)_{19}$ (**67**)	polymer C_{70}^{3-}	–	124
$\{K^+(THF)_5\}(C_{60}^{-\bullet})(THF)_2$ (**68**)	monomeric $C_{60}^{-\bullet}$	linear chains, $r = 9.86$ Å, $N = 2$	73
$K_3^+(C_{60}^{3-})(THF)_{14}$ (**69**)	monomeric C_{60}^{3-}	isolated C_{60}^{3-}, $r = 12.9$ Å	80
$Na^+(C_{60}^{-\bullet})(THF)_5$ (**70**)	monomeric $C_{60}^{-\bullet}$ at room temperature	strong antiferromagnetic interactions at $T > 200$ K ($\mu_{ef} = 1.7\ \mu_B$, $\theta = -56$ K), dimerization at $T < 200$ K	81
$K_3C_{60}(THF)_7$ (**71**)	–	–	82
$(Na^+)_x(THF)_y(C_{60}^-)$ (**72**) ($x = 0.39 \pm 0.03$, $y = 2.2 \pm 0.7$)	partial charge transfer, $C_{60}^{0.4-}$	$\sigma = 50$ S cm^{-1} (see [b]), metal, conversion to dielectric at $T < 180$ K	84, 85
$(Li^+)_x(THF)_y(C_{60}^-)$ (**73**)	partial charge transfer	$\sigma = 30$ S cm^{-1} (see [b]), semiconductor	86
$\{Co^{2+}(DMF)_{3.3}\}(C_{60}^{-\bullet})_2$ (**74**)	monomeric $C_{60}^{-\bullet}$	$\theta = -48$ K, $\sigma = 6$ S cm^{-1} (rt),[c] semiconductor	196
$\{Ni^{2+}(DMF)_4\}(C_{60}^{-\bullet})_2$ (**75**)	the same	$\theta = -49$ K	196
$\{Fe^{2+}(DMF)_4\}(C_{60}^{-\bullet})_2$ (**76**)	"	$\theta = -17$ K, $\sigma = 0.25$ S cm^{-1} (rt),[c,d] semiconductor	196
$\{Mn^{2+}(DMF)_{3.5}\}(C_{60}^{-\bullet})_2$ (**77**)	dimerization	transition $2\,C_{60}^{-\bullet} \rightleftarrows (C_{60}^-)_2$ at 240–160 K, $\sigma = 0.14$ S cm^{-1} (rt)[c]	196
$\{Eu^{2+}(DMF)_4\}(C_{60}^{-\bullet})_2$ (**78**)	"	transition $2\,C_{60}^{-\bullet} \rightleftarrows (C_{60}^-)_2$ at 200–150 K	196
$\{Cd^{2+}(DMF)_{2.5}\}(C_{60}^{-\bullet})_2$ (**79**)	monomeric $C_{60}^{-\bullet}$	$\sigma = 0.6$ S cm^{-1} (rt),[c] semiconductor	196

[a] Here and below, a formula unit is given for polymeric structures; [b] the electrical conductivity was measured for a single crystal; [c] the electrical conductivity was measured for a pressed pellet; [d] here and in Table 9, rt is room temperature.

conductor type. At 150 K, phase transition occurs, resulting in a decrease in the conductivity; the nature of this transition is unknown.[86] Compounds **72** and **73** are the first examples of ionic compounds of fullerene with partial charge transfer that are highly conductive.

The salts $\{M^{2+}(DMF)_y\}(C_{60}^{-\bullet})_2$ ($y = 2.4-4$; M = Co, Ni, Fe, Mn, Eu, Cd) (**74**–**79**) were prepared under anaerobic conditions by the cation metathesis of $Cs^+C_{60}^{-\bullet}$ with the metal salts MX_2 (X = Cl, Br, I) in DMF (as black or dark brown polycrystalline powders). Salts **74**–**79** are poorly soluble in DMF and precipitate from concentrated solutions. The IR, Vis and near-IR spectroscopy data attest to the radical anion state of fullerene in these salts.[196]

A study of the magnetic behaviour of fullerene salts **74**–**76** with paramagnetic cation [Co^{2+} (**74**), Ni^{2+} (**75**) and Fe^{2+} (**76**)] has shown the presence of strong antiferromagnetic interactions, as the Weiss temperature is negative: −49, −48 and −17 K for salts **74**, **75** and **76**, respectively.

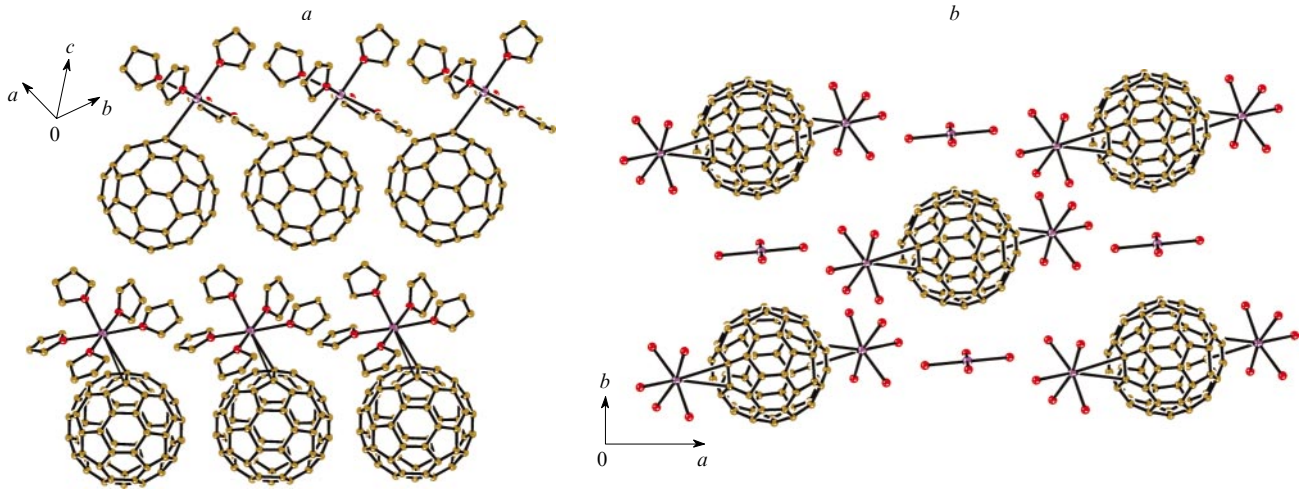


Figure 15. Linear fullerene chains of $C_{60}^{-\bullet}$ radical anions in the ionic complex $\{K^+(THF)_5\}C_{60}^{-\bullet}(THF)_2$ (**68**) (*a*),[80] packing of C_{60}^{3-} trianions in the ionic complex $K_3^+(C_{60}^{3-})(THF)_{14}$ (**69**) (*b*).[79]
Instead of the THF molecule, only the oxygen atom that is coordinated by the potassium cation is shown.

This is probably responsible for the unusual EPR behaviour of these salts. All three salts show signals with the *g*-factors of 1.9918 – 1.9955 and ΔH = 5.6 – 12.6 mT, which can be assigned to $C_{60}^{-\bullet}$. As the temperature decreases, the signals due to $C_{60}^{-\bullet}$ are substantially broadened to the maximum value of 40 mT (compound **75**, 6 K), the *g*-factors shift to 1.992 – 1.965, and the integrated intensity of the EPR signal decreases at $T < 6$ K. All these effects may be caused by the strong antiferromagnetic interaction between $C_{60}^{-\bullet}$ and paramagnetic metal cations.[196]

Fullerene salts with $Mn^{2+}(DMF)_{3.5}$ (**77**) and $Eu^{2+}(DMF)_4$ (**78**) cations show a different behaviour. They show two EPR signals, which can be assigned to the $C_{60}^{-\bullet}$ anions and Mn^{2+} and Eu^{2+} cations. The EPR signal due to $C_{60}^{-\bullet}$ disappears in the range of 200 – 150 K and the magnetic moment decreases with a decrease in temperature due to removal of the contribution of the $C_{60}^{-\bullet}$ spins. This transition can be attributed to the formation of diamagnetic $(C_{60}^{-})_2$ dimers. In the phase containing the dimers, the paramagnetic $Mn^{2+}(DMF)_{3.5}$ and $Eu^{2+}(DMF)_4$ cations are magnetically isolated as the Weiss temperature of salts **77** and **78** is close to zero at $T < 150$ K. The transition to the diamagnetic $Cd^{2+}(DMF)_{2.5}$ cation in salt **79** results in the magnetic isolation of $C_{60}^{-\bullet}$. Thus, for magnetic interactions to occur, it is important that unpaired spins be present in both the fullerene radical anion and the metal cation.[196]

The conductivity of the salts was measured for pressed pellets by the four-contact method under anaerobic conditions. Even a powdered sample of salt **74** has a high ($\sigma = 6$ S cm^{-1}) electrical conductivity at room temperature; for salts **79**, **76** and **77**, it is somewhat lower (0.6, 0.26 and 0.14 S cm^{-1}, respectively). All salts have a semiconductor-type conductivity with activation energy of 40 – 100 meV.[196]

7. Metallic conductivity in layered multicomponent compounds

Compounds with high electrical conductivity can be obtained only in the case of close packing of fullerene anions in the crystal; meanwhile, these anions tend to dimerize (when there are short contacts between them). This problem can be solved by introducing neutral component D, which separates fullerenes and prevents their dimerization.

As such component, the aromatic hydrocarbon triptycene (TPC) was chosen.[147] In the complex $(MDABCO^+)\cdot(C_{60}^{-\bullet})TPC$ (**80**), it forms hexagonal layers with voids, which accommodate small $MDABCO^+$ cations (Fig. 16 *c*). The $C_{60}^{-\bullet}$ radical anions partially reside in the voids of the $TPC-MDABCO^+$ layer, thus providing the formation of hexagonal fullerene layers, and also the fulleride anions are separated by TPC molecules, which rules out dimerization. In structure **80**, the fullerene layers alternate with the $TPC-MDABCO^+$ layers along the [001] direction (Fig. 16 *a*). Each fulleride anion has six neighbours in a layer (Fig. 16 *b*) with an intercentre distance of 10.073 Å, giving rise to numerous van der Waals C···C contacts between them.[147]

At room temperature, fulleride anions are ordered in one layer (type I layers) but are disordered over three orientations in another layer (see Fig. 16 *a*, type I and II layers). This difference is caused by their different environments in these layers. In type I layers, fullerene cores are located closely to neutral TPC molecules, whereas in type II layers, they are proximate to the $MDABCO^+$ cations (see Fig. 16 *a*). The $C_{60}^{-\bullet}$ radical anions are ordered in type II layers at 210 – 200 K. The phase transition resulting in ordering of all components and appearance of slight asymmetry in the fullerene layers occurs in complex **80** at 183 K.[147]

The electrical conductivity of complex **80** measured by the four-contact method for single crystals is 4 S cm^{-1} at room temperature and increases as temperature decreases, *i.e.*, gives a metallic-type behaviour (34 S cm^{-1} at 150 K). The complex gives an asymmetric Dysonian shape EPR signal typical of highly conductive compounds, and magnetic measurements show a substantial contribution of the temperature-independent Pauli susceptibility (inherent in metals). At low temperatures ($T < 100$ K), the conductivity cannot be measured correctly as the contact resistance sharply increases. Nevertheless, magnetic measurement

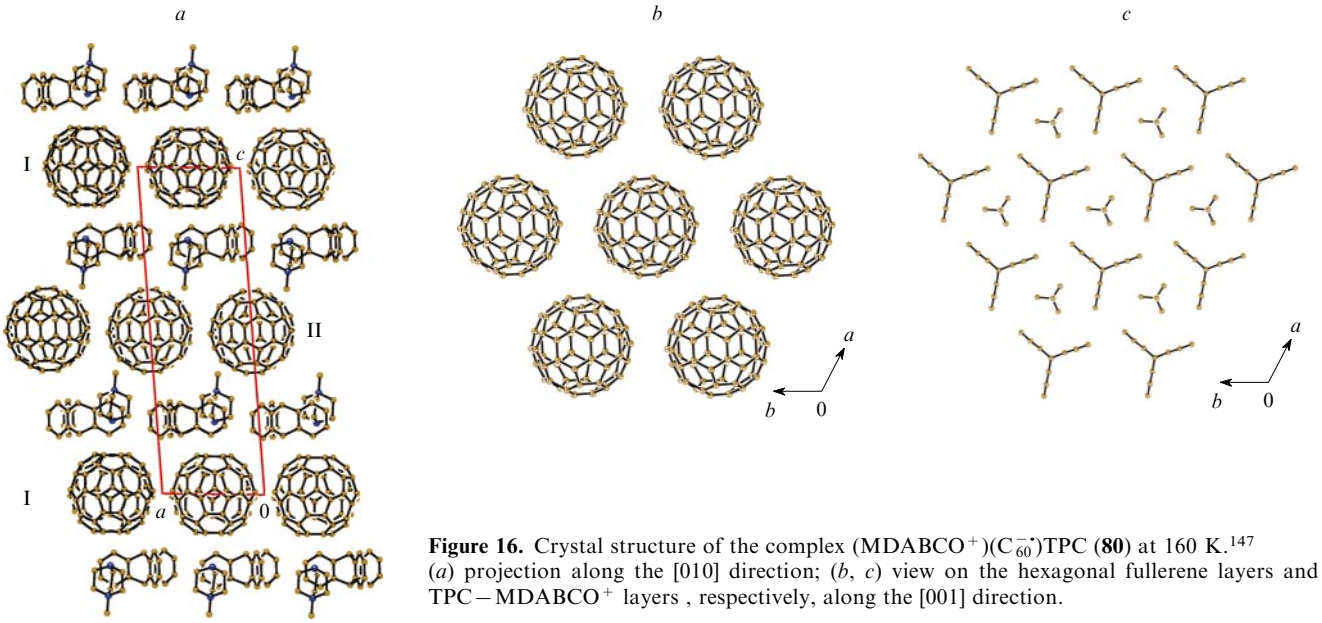


Figure 16. Crystal structure of the complex $(MDABCO^+)(C_{60}^{-\bullet})TPC$ (**80**) at 160 K.[147] (*a*) projection along the [010] direction; (*b*, *c*) view on the hexagonal fullerene layers and $TPC-MDABCO^+$ layers , respectively, along the [001] direction.

data indicate that compound **80** should be a metal down to 4 K. We believe that the conductivity of type I and II fullerene layers differs in the range of 220–360 K, as the ordered layer is metallic and the disordered layer is non-metallic and involves antiferromagnetic spin coupling. After ordering of fullerenes in type II layers at 210–200 K, these layers also pass to the metallic state, and, hence, at $T < 200$ K both fullerene layers show metallic-type conductivity.[147]

8. Salts of chemically modified fullerenes

Halofullerenes are most frequently encountered and most studied fullerene derivatives. However, during chemical reactions they lose halogen atoms and do not form ionic compounds.[52,53] As opposed to halofullerenes, derivatives in which addends are attached to the fullerene cage through C–C bonds are usually form stable anions. For these derivatives, ionic compounds have been obtained; some of them demonstrated interesting properties. The attached exopolyhedral fragments prevent the rotation of fullerene spheres, thus facilitating determination of their crystal structure. Meanwhile, the addition of addends to the fullerene cage reduces the symmetry of molecule. Since the conductive and superconductive properties of fullerides are largely determined by high (I_h) symmetry of C_{60} and degeneracy of its LUMO,[197] removal of the degeneracy of molecular orbitals has an adverse effect on the conductivity. The preparation of high-quality single crystals of ionic compounds of chemically modified fullerenes also remains a challenge, most of the studies of the properties of these compounds being performed using powders.

Most interesting are the works dealing with reduction of $C_{60}CH(m\text{-}O_2NC_6H_4)$ and $C_{60}CH(m\text{-}H_2NC_6H_4)$ with cobaltocene (compounds **81** and **82**, respectively).[198–201] Cobaltocene reduces fullerene derivatives, and the resulting ionic compounds $(CoCp_2)^+[C_{60}CH(m\text{-}RC_6H_4)^{-\bullet}]$ precipitate from toluene as powders. It follows from the optical spectra that full charge transfer occurs in these compounds to give fullerene radical anions. The magnetic measurements are indicative of the ferromagnetic spin ordering in compounds **81** and **82** at $T < 19$ K. This is a very interesting fact considering that the $(CoCp_2)^+$ cation is diamagnetic and, hence, the magnetism in these compounds is due only to the spins concentrated on the carbon cage. However, in the known $(TDAE^{+\bullet})C_{60}^{-\bullet}$ ferromagnet,[11] the spins are present both in the $C_{60}^{-\bullet}$ anion and the $TDAE^{+\bullet}$ cation.

In the ionic compound, $(CoCp_2)^+[C_{60}CH(XC_6H_4)^{-\bullet}]$, in which an NO_2 or NH_2 group is located in the *ortho*- or *para*-position, only antiferromagnetic spin couplings are observed down to 4 K.[198,199] Antiferromagnetic spin coupling was also detected in the ionic compounds $C_{60}C(CO_2Et)_2$ and $C_{70}C(CO_2Et)_2$ with cobaltocene and TDAE.[198]

A series of studies were performed with dicyanofullerene $C_{60}(CN)_2$.[48,54,55,184] This derivative is reduced more readily than the initial fullerene;[48] however, the reducing agents (dibenzenechromium, cobaltocene, potassium/dibenzo-18-crtown-6 in THF) are almost the same as for C_{60}.[54,55] In the ionic multicomponent complex, $\{Cr^{I}(C_6H_6)_2^{+\bullet}\}_2[Co^{II}TPP\{C_{60}(CN)_2^-\}]\{C_{60}(CN)_2^{-\bullet}\}(C_6H_4Cl_2)_3$ (**42**), the structure of the $C_{60}(CN)_2^{-\bullet}$ radical anion was determined for the first time.[184] The optical spectra indicate that the negative charge is substantially delocalized on the cyano groups, which induces a shift of the C≡N band in the IR spectra. It was shown that in $\{Cr^{I}(C_6H_6)_2^{+\bullet}\}C_{60}(CN)_2^{-\bullet}$ (**83**), the $C_{60}(CN)_2^{-\bullet}$ radical anions can dimerize, and the dimers start to dissociate only at $T > 380$ K, which is markedly higher than the temperature at which dissociation of the $(C_{60}^-)_2$ dimer linked by one C–C bond starts (130–280 K). Apparently, it is the charge delocalization on the cyano groups resulting in a decrease in the repulsion of negative charges in $\{C_{60}(CN)_2^-\}_2$ that considerably stabilizes the dimeric state.[55]

9. Salts with positively charged fullerenes

Unlike numerous compounds with fulleride anions, only a few compounds with a positive charge on the carbon cage have been obtained as yet. This is related to both high oxidation potentials of fullerenes (see Section II) and their ability to easily add various nucleophiles, which could serve as oxidants, for example, Cl_2 and Br_2. The range of compounds for the oxidation of fullerenes is limited to only very weak nucleophiles. The interest in compounds with fullerene cations is very high. The reason is that radical cation compounds of fullerenes may be expected to exhibit unique conducting properties including high-temperature superconductivity,[202,203] because the HOMO of C_{60} is five-fold degenerate, unlike the three-fold degenerate LUMO. The first ionic compound $(C_{60}^{2+})(SbF_6^-)_2$ with a fullerene dication was obtained by oxidation of C_{60} with the strong SbF_5 oxidant in liquid SO_2. It was isolated as a powder, and its structure was refined by the Rietveld method.[53] It was found that the fullerene dications in this compound form an unusual zigzag-shaped polymer. Apparently, due to polymerization, the compound does not exhibit conducting or magnetic behaviour, although these are predicted theoretically for cationic C_{60} derivatives.[202,203] This compound is diamagnetic and is a semiconductor with a moderate activation energy (80 mEv).[60] One cationic compound of C_{70} with a complex titanium-containing anion, $(C_{70}^+)_2(Ti_3Cl_{13}^-)_2$, is known. It was prepared by the reaction of $C_{70}Br_{10}$ with $TiCl_4$ in a sealed tube at 60–80 °C over a period of 1–2 days. This compound is a very strong oxidant, as it oxidizes Br^- to molecular bromine, and is slowly hydrolyzed in air.[61]

V. The molecular and electronic structure of monomeric, dimeric and polymeric fullerene anions

1. Characteristic features of the electronic structure of monomeric fulleride anions

The highest occupied molecular orbital of fullerene C_{60} is the h_u level; it is five-fold degenerate and fully occupied by ten electrons. The lowest unoccupied molecular orbitals (LUMO and LUMO + 1) are the three-fold degenerate t_{1u} and t_{1g} levels, respectively.[204] The high degree of degeneracy is caused by the high symmetry of the C_{60} molecule. The degeneracy was found to have the decisive influence on the conductive properties of fullerene derivatives.[204] This accounts for the fact that factors reducing the symmetry of the C_{60} molecule, for example, the Jahn–Teller effect, considerably affect the properties of fullerene compounds.

The reduction of fullerene results in polulation of the t_{1u} levels of the conduction band, each of them being able to accommodate up to six electrons. The resulting ionic C_{60} compounds may develop high conductivity or even superconductivity.[14,32,37] Depending on the degree of fullerene

reduction, the type of conductivity sharply changes, which is determined by popupation of the t_{1u} level.

The transfer of one electron affords the $C_{60}^{-\cdot}$ radical anion. The presence of the unpaired electron is responsible for the fact that compounds of $C_{60}^{-\cdot}$ can exhibit conductive properties and magnetic spin ordering when there are sufficiently short contacts between fullerene radical anions. The effective magnetic moment of salts containing the $C_{60}^{-\cdot}$ anions are $\mu_{ef} = 1.65-1.80$ μ_B at room temperature, which corresponds to a doublet ground state with the spin $S = 1/2$.[73,81,116,127]

The transfer of two electrons on fullerene produces the C_{60}^{2-} dianion. With retention of the high symmetry (I_h) of the molecule [proceeding from the Hund's rule for the $(t_{1u})^2$ configuration], a triplet ground state with two unpaired electrons is expected (Fig. 17 *a*, I_h). Due to the Jahn–Teller effect or other effects (for example, an asymmetric local environment of fullerene or interactions with cations), the symmetry of the C_{60} molecule may decrease. Upon an ellipsoidal distortion of the shape of the carbon cage, this should remove the degeneracy of the t_{1u} orbital to give at least two levels: *a* and *e* differing by ΔE in energy, as shown in Fig. 17 *a*. According to calculations, upon this splitting, the singlet state will be the ground state and the triplet state will be the excited state being separated from the former by ΔE (see Fig. 17 *a*, singlet).[205,206] If ΔE is comparable with kT (k is the Boltzmann constant), the excited triplet level can be populated at higher temperature (see Fig. 17 *a*, triplet). However, if ΔE is great, the dianion will still remain diamagnetic even at room temperature. The ΔE value can be quantitatively estimated from EPR data. The molecular orbital calculations for the C_{60}^{2-} dianion indicate that the triplet excited state is separated from the singlet ground state by 300–1500 cm^{-1} (Refs 205 and 206). For most C_{60}^{2-} salts, only X-ray diffraction data are available, which in some cases show ellipsoidal distortions of the fullerene cage [76,117–121,151] related presumably to the Jahn–Teller effect. The salt $(PPN^+)_2(C_{60}^{2-})$ (**24**) studied by EPR in DMSO exhibits no signals in the range of 125–280 K, except for a narrow impurity signal; this allowed the authors to draw conclusion about a diamagnetic ground state of C_{60}^{2-} (Ref. 207). In another work, the electrochemically generated C_{60}^{2-} dianion in DMSO was also found to exhibit only a narrow impurity signal at low temperatures, but at $T > 135$ K, a new signal appeared in the EPR spectrum, and its intensity increased with temperature, which provided the grounds for assigning it to the triplet state whose population increases with temperature.[208] The diamagnetic ground state of the C_{60}^{2-} dianion was confirmed by SQUID measurements and EPR spectroscopy for the complex $(CoCp_2^*)_2^+(C_{60}^{2-})(C_6H_4Cl_2,PhCN)_2$ (**16**), which was prepared as crystals. In this case, the appearance of a new broad EPR signal at $T > 140$ K was also attributed to population of the closely lying triplet level.[179,180] The effective magnetic moments of the salts containing C_{60}^{2-} dianions at room temperature are 1.0–2.3 μ_B for various samples of salt **26**[73] and 1.29 μ_B for salt **32**.[76] These values are much lower than could be expected of an anion with the triplet ground state ($S = 1$, $\mu_{ef} = 2.83$ μ_B). Moreover, the magnetic moment of these salts considerably decreases as temperature decreases.[73,76] Complex **16** is diamagnetic at low temperature, the increase in the magnetic susceptibility at $T > 140$ K being probably caused by population of the excited triplet level.[172,173] Thus, the C_{60}^{2-} dianion has a diamagnetic singlet ground state, and in some cases, the excited triplet level is also populated.

The C_{60}^{3-} trianion is most interesting, because salts M_3C_{60} are metals and can pass to the superconducting state.[14,32,37] The electron state of the C_{60}^{3-} trianion in the absence of fullerene cage distortions can be a quartet ($S = 3/2$). This state is formed if C_{60}^{3-} with the $(t_{1u})^3$ configuration obeys Hund's rule (Fig. 17 *b*, I_h). However, when there are distortions, the t_{1u} orbital should be split into at least two levels (*a* and *e*) and the quartet should turn into a doublet ($S = 1/2$, Fig. 17 *b*, doublet). Only in one publication,[209] an EPR spectrum that can be interpreted as a quartet was recorded for the C_{60}^{3-} trianion. Subsequently these data have not been confirmed and the observed spectrum was assigned to the reduction of the impurity of $C_{120}O$, which may be present in the initial fullerene.[207] The main bulk of experimental data indicate that C_{60}^{3-} trianions tend to slightly deviate from I_h symmetry.[74,75] The effective magnetic moments of C_{60}^{3-}-derived salts ($\mu_{ef} = 1.73-1.80$ μ_B) indicate unambiguously the presence of only one spin ($S = 1/2$) in this anion.[73–75]

The tetraanions of C_{60} fullerene are difficult to chemically prepare, as they are formed only at large negative potentials (< -2.35 V *vs.* Fc/Fc^+).[13] So far, only one salt with the C_{60}^{4-} tetraanion was obtained (by direct synthesis) in solution and characterized in the solid state.[72] The EPR data for this salt indicate that at low temperatures, the tetraanion does, most likely, produce no EPR signal and, hence, has a singlet ground state ($S = 0$). However, based on the ^{13}C NMR data, it is assumed that at room temperature, the triplet excited level of the tetraanion can be populated. Generally, the electronic structure of tetraanions should resemble the electronic structure of C_{60}^{2-} dianions. Unlike the metallic M_3C_{60} phases, the M_4C_{60} phases are semiconductors with moderate ($\sim 30-100$ meV) activation energy.[210] One possible reason for this behaviour is the Jahn–Teller splitting of the t_{1u} orbital to give the low-spin states in which two lower levels are fully occupied and the upper level is vacant. One more possible reason is the repulsion of electrons, giving rise to a Mott–Hubbard insulator.[211,212] Recently, single crystals of Rb_4C_{60} were

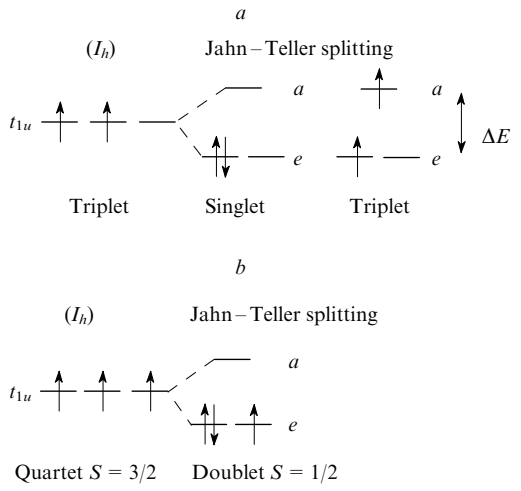


Figure 17. Jahn–Teller splitting of the LUMO in the C_{60}^{2-} dianion (*a*) and C_{60}^{3-} trianion (*b*).

obtained for the first time, which made it possible to structurally characterize the C_{60}^{4-} tetraanion.[213]

More reduced compounds of C_{60}, for example, M_5C_{60} phases can be obtained by doping of fullerene by alkali metals in ammonia. Presumably, the C_{60}^{5-} pentaanion should resemble the $C_{60}^{-\bullet}$ radical anion, *i.e.*, it should have one unpaired spin in the LUMO ($S = 1/2$). In the M_6C_{60} salts, the t_{1u} orbital is fully occupied by six electrons; all M_6C_{60} compounds are dielectric.[214]

When more than six electrons have been added to the C_{60} molecule, the t_{1g} level, which can accept six more electrons, starts to be populated. Therefore, for degrees of fullerene reduction of $6 < x < 12$, the metallic state can again develop in C_{60} compounds and transitions to the superconducting state are possible.[14, 32, 215]

The electronic structures of anions of other fullerenes have been less studied. The fullerene C_{70} and higher fullerenes (C_{76}, C_{78}, C_{84}) have lower symmetry; therefore, the LUMO of these fullerenes are no longer degenerate and the distortions of the fullerene cage do not affect significantly their electronic structure and properties. An exception is provided by one C_{84} isomer with D_{2d} symmetry. EPR data suggest a doubly degenerate LUMO, as the spectral pattern of C_{84}^{2-} dianions is very similar to that of the C_{60}^{2-} dianions. They also have a singlet ground state, and the triplet excited state is accessible at elevated temperatures. The signal of the triplet increases with temperature; using this dependence, the ΔE value between the singlet and triplet levels was estimated [216] as 180 cm^{-1}.

2. Molecular structures and properties of charged fullerene dimers

In ionic complexes and salts, in the presence of short contacts between fullerenes, the $(C_{60}^-)_2$ dimers linked by one C–C bond are formed. They have C_{2h} symmetry with *trans*-positions of C_{60}^- anion (Fig. 18 *a*). The C–C bond length between the carbon cages [1.587(4)–1.597(7) Å] [100, 128, 145, 178] is much longer than the usual C–C bond length between sp^3-hybridized carbon atoms [1.541(3) Å].[217] The distance between the fullerene centres in the dimer is 9.25–9.32 Å.[100, 128, 145, 178] The dimers are diamagnetic; thus, their formation is accompanied by transition of the compound from the paramagnetic to diamagnetic state or by a decrease in the magnetic moment.[100, 101, 128, 178, 218]

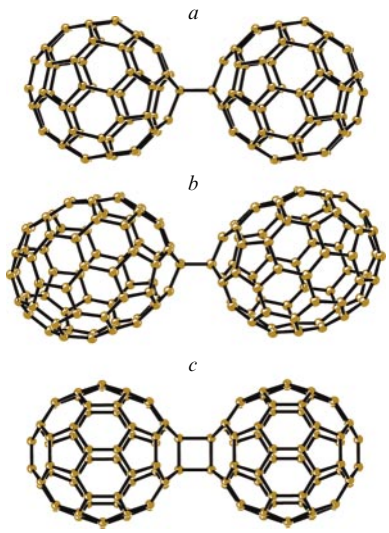


Figure 18. Molecular structures of fullerene dimers.
(*a*) $(C_{60}^-)_2$ linked by one C–C bond in complex **10**;[100] (*b*) $(C_{70}^-)_2$ linked by one C–C bond in complex **2**;[163] (*c*) $(C_{60}^-)_2$ linked by two C–C bonds in complex **50**.[188]

The $C_{70}^{-\bullet}$ radical anions also dimerize to give $(C_{70}^-)_2$ dimers with one exopolyhedral C–C bond (Fig. 18 *b*).[163, 193, 218, 219] Dimerization of $C_{70}^{-\bullet}$ takes place almost in all anionic compounds of fullerene C_{70} known to date. The only exception is the salt $(Ph_4P^+)_2(C_{70}^{-\bullet})I^-$ (**21**) in which the $C_{70}^{-\bullet}$ radical anions are monomeric down to helium temperatures due to long distances between them.[67] Dimers have C_{2h} symmetry, which is much lower than the symmetry of the initial C_{70} fullerene (D_{5h}). The molecular structure of the $(C_{70}^-)_2$ dimers was determined most precisely for complexes **2** and **3** (Fig. 18 *b*). The C_{70}^- anions in the dimer are *trans*-arranged, the C–C bond between them is 1.583(2)–1.586(3) Å long and the distance between the centres of C_{70}^- is 10.47–10.51 Å.[163, 193, 218, 219] The C–C bond between the fullerene cages in $(C_{70}^-)_2$ is much shorter than that in $(C_{60}^-)_2$ but markedly longer than the length of the usual C–C bonds. The $(C_{70}^-)_2$ dimers are diamagnetic.[163, 193, 218, 219]

The $C_{70}^{+\bullet}$ radical cations in the compound $(C_{70}^+)_2(Ti_3Cl_{13}^-)_2$ dimerize to give the $(C_{70}^+)_2$ dimers with one exopolyhedral C–C bond.[61] The geometry of this dimer resembles that of the negatively charged $(C_{70}^-)_2$ dimer (see Fig. 18 *b*). The C_{70}^+ cations occupy *trans*-positions, the C–C bond length between them being 1.616(4) Å.

The neutral $(C_{60})_2$ dimer linked by two C–C bonds has been known quite for long. It is formed in the mechanochemical reaction of C_{60} with KCN.[220] As it is formed, two π-bonds in the fullerene are opened and a cyclobutane ring is formed. The negatively charged $(C_{60}^-)_2$ dimers linked by two C–C bonds have been unknown until recently. The reduction of the neutral $(C_{60})_2$ dimer gives rise to the dimeric $(C_{60})_2^{-\bullet}$ radical anion, which immediately dissociates in solution to neutral C_{60} and the $C_{60}^{-\bullet}$ radical anion.[221] Recently, $(C_{60}^-)_2$ dimers linked by two C–C bonds (see Fig. 18 *c*) were found in ionic complexes **50** and **51**.[188–190] The dimer in complex **50** has D_{2h} symmetry, the C–C bond length between the fullerene cages being 1.581(3) Å, the distance between their centres being 9.07 Å.[188] The dimer in structure **51** has longer C–C bonds between the C_{60}^- [1.607(6) Å] cages [190] but in this case, the accuracy of structure determination is lower than for complex **50**. It can be seen that the distance between the centres of the fullerene cages in these dimers is much longer than in the $(C_{60}^-)_2$ dimer with one exopolyhedral C–C bond, whereas the bond lengths between the C_{60} cages remain almost unchanged.

As opposed to diamagnetic $(C_{60}^-)_2$ dimers linked by one C–C bond, the $(C_{60}^-)_2$ dimers with two bonds have unpaired spins at room temperature.[188–190] These dimers in structure **51** are magnetically isolated by diamagnetic porphyrins ZnTMPP,[190] whereas the paramagnetic dimers and Co^{II}TMPP in structure **50** undergo strong magnetic coupling.[188] The magnetic moment of complex **51** is 2.69 μ_B at room temperature, which is closer to the value of 2.83 μ_B typical of the triplet ($S = 1$) than to the value of 2.45 μ_B, which is expected for a system of two non-interacting spins

$s = 1/2$. The magnetic chartacteristics of this dimer are adequately described by the Ginzburg model for a pair of isolated antiferromagnetically coupled spins with $J/k = -44.7$ K. A drop of the magnetic susceptibility of complex **51** occurs at $T < 40$ K, which is indicative of the diamagnetic ground state of the dimer.[185] This diamagnetism is apparently caused by strong antiferromagnetic spin coupling in the dimer, while diamagnetism of the $(C_{60}^{-})_2$ dimer linked by one C–C bond is a result of the existence of this bond and is observed over the whole temperature range of existence of the dimer. The $(C_{60}^{-})_2$ dimers with two bonds in complex **51** yield a narrow EPR signal with a Loretnzian shape with $g = 2.0014$ at room temperature. The intensity of this signal sharply drops at $T < 40$ K. The sample becomes magnetically diluted and at low temperature it is possible to observe the triplet splitting of the EPR signal. The dipole coupling constant is 2.6 mT and the averaged distance between the spins is 10.2 Å.[190] These parameters are similar to the parameters of another negatively charged dimer, $C_{120}O^{2-}$ (Refs 207 and 222).

3. Properties of polymers composed of fullerene anions and cations

The intercalation of C_{60} with alkali metals in 1 : 1 stoichiometric ratio gave radical anion salts KC_{60}, RbC_{60} and CsC_{60}.[223–225] On slow cooling of the intercalation products, [2 + 2]-cycloaddition takes place for neighbouring fullerene molecules resulting in $C_{60}^{-\bullet}$ polymerization to give linear chains (Fig. 19 *a*). The distance between the centres of the fullerene cages decreases from 9.9 to 9.11–9.13 Å upon polymerization.[223] The polymers are stable in air, insoluble in tetrahydrofuran and depolymerize only on heating above 320 °C. A study of the electrical conductivity of the polymeric samples has shown that $(KC_{60})_n$ is a 3D metal: as temperature decreases, its conductivity slowly increases up to 4 K.[223] According to magnetic measurements, $(KC_{60})_n$ also behaves as a 3D metal down to helium temperatures. The polymers $(RbC_{60})_n$ and $(CsC_{60})_n$ are one-dimensional metals and pass to the dielectric state at 50 and 40 K, respectively. In the polymeric chains of these compounds, a magnetic transition with antiferromagnetic spin ordering takes place at 25 K (so-called antiferromagnetic spin density waves arise).[224, 225]

On fast cooling with liquid nitrogen, C_{60} doped with alkali metals has not time to polymerize, and monomeric radical anion salts, RbC_{60} and CsC_{60}, are formed. On heating of RbC_{60} above 125 K or CsC_{60} above 150 K, dimerization of $C_{60}^{-\bullet}$ takes place; the dimer-containing phase is dielectric.[229–232] According to X-ray powder diffraction data, these phases were found to contain $(C_{60}^{-})_2$ dimers linked by one C–C bond. Subsequently these dimers were found in ionic compounds of fullerenes with metallocenes and some other cations.[100, 101, 128, 145, 177, 178]

It was shown that in some compounds such as Na_2RbC_{60},[226] Na_2CsC_{60},[233] and Li_3CsC_{60},[234] the C_{60}^{3-} trianions also polymerize. Even under moderate pressure, the structure transforms from simple cubic to monoclinic; this gives a linear polymer in which every fullerene forms one new C–C bond with neigbouring fullerenes (Fig. 19 *b*). The distances between the centres of fullerenes in this polymer are ~9.38 Å.[226, 233, 234] The initial phases with the monomeric C_{60}^{3-} trianion are superconducting. It was assumed that polymerization reduces the transition temperature to the superconducting state in Na_2CsC_{60} by about 3 K, and the Na_2RbC_{60} phase apparently does not pass to the superconducting state but remains a metal or, alternatively, the temperature of this transition is too low.[233]

The reduction of fullerene C_{70} by alkaline earth metals and lanthanides in liquid ammonia provided zigzag $(C_{70}^{2-})_n$ and $(C_{70}^{3-})_n$ polymers in which every C_{70}^{n-} anion is connected to the neighbouring one by a single C–C bond (Fig. 19 *c*). The properties of these polymers have not yet been sufficiently studied.[122–124]

The structure of Na_4C_{60} salts is composed of polymeric $(C_{60}^{4-})_n$ layers in which each fullerene cage forms four new single C–C bonds with neighbouring cages (Fig. 19 *d*). It was shown [227] that this polymer is a highly correlated metal but it does not pass to the superconducting state.

Polymeric layers of a different type are already formed in the Li_4C_{60} salts at room temperature.[228, 235] They are composed of fullerene chains formed according to the [2 + 2]-cycloaddition pattern similarly to the polymers in

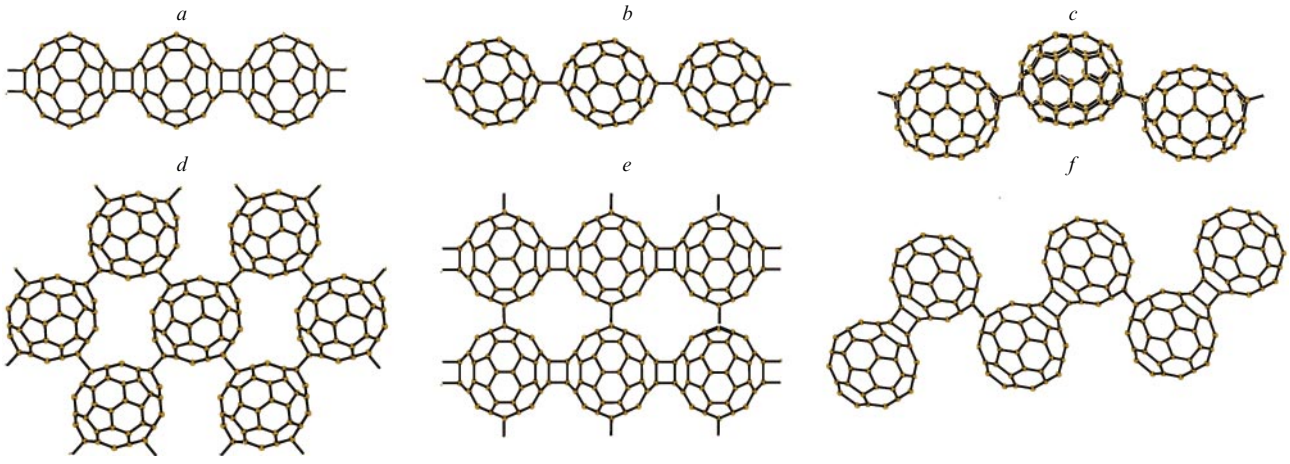


Figure 19. Linear $(C_{60}-)_n$ polymer in the structures MC_{60} (M = K, Rb and Cs) (*a*);[223–225] linear polymer of $(C_{60}^{3-})_n$ trianions in Na_2RbC_{60} (*b*);[226] polymer of $(C_{70}^{2-})_n$ dianions in $\{Sr^{2+}(NH_3)_8\}C_{70}^{2-}(NH_3)_3$ (**66**) (*c*);[122] polymeric layer of $(C_{60}^{4-})_n$ tetraanions in Na_4C_{60} (*d*);[227] polymeric layer of $(C_{60}^{4-})_n$ tetraanions in Li_4C_{60} (*e*);[228] zigzag polymer of $(C_{60}^{2+})_n$ dications in $(C_{60}^{2+})(SbF_6^{-})_2$ (*f*).[60]

the MC_{60} salts. The chains are connected by single C–C bonds to form a layer (Fig. 19 *e*). In terms of the electronic characteristics, this polymer refers to non-magnetic dielectrics;[235] however, this phase exhibits high ionic conductivity implemented by means of high mobility of lithium cations.[236]

Fullerene cations also tend to polymerize. In 2010, the first zigzag polymer of $(C_{60}^{2+})_n$ dications in the $C_{60}^{2+}(SbF_6^-)_2$ salt was obtained.[60] In this polymer, each fullerene cage is linked by two C–C bonds to one neighbour and by only one C–C bond to the other neighbour (Fig. 19 *f*). The polymer is a semiconductor with the diamagnetic ground state.[60]

VI. Characteristic features of the crystal structure

Theoretical calculations indicate[237] that the reduction of fullerenes should lead to a change in the bond lengths in the molecule. This is caused by the nature of the t_{1u} orbital, which is antibonding with respect to the [6,6]-bonds and bonding with respect to the [6,5]-bonds. As the charge on the fullerene molecule increases, the [6,6]- and [6,5]-bond lengths should become equal and the fullerene sphere should be distorted to form an ellipsoid. Table 7 summarizes the experimentally determined average bond lengths in a neutral C_{60} fullerene molecule, molecular and ionic compounds of fullerenes with different anion charge. We specially chose only crystal structures solved with a good accuracy. It can be seen that an increase in the charge on the fullerene cage entails some change in the bond lengths but these changes are minor and in most cases, they are within experimental error.

In terms of positions of the C_{60} anions in the crystal and the number of direct van der Waals contacts between them, several structural types of ionic compounds of fullerenes can be distinguished.[241, 242]

1. Three-dimensional close packing of fulleride anions with distances between the C_{60} centres of 9.8–10.3 Å has been observed so far only in M_xC_{60} salts ($x = 1–6$) with alkali and alkaline earth metals. The number of C_{60}^{n-} close neighbours varies in these structures from 12 to 8.[14, 28]

2. Layered packing comprising two-dimensional tetragonal or hexagonal layers of C_{60} anions. The number of close neighbours in such layer is 4 for tetragonal and 6 for close-packed hexagonal layers. The hexagonal fullerene layers can also be constructed according to the honeycomb pattern and involve large voids; in this case, each fulleride anion has only three neighbours. Loose tetragonal layers are formed in the compound $(NiCp_2^*)^+(C_{60}^{-\bullet})CS_2$ (**4**),[106] close-packed hexagonal layers are formed in $(Me_4N^+)C_{60}^{-\bullet}(THF)_{1.5}$ (**38**) and $(MDABCO^+)(C_{60}^{-\bullet})TPC$ (**80**).[116, 147] Hexagonal layers having voids were found in the complexes $[Mn^{II}Pc(EtS^-)_x(I^-)_{1-x}]C_{60}^{-\bullet}(PMDAE^+)_2 .C_6H_4Cl_2$ ($x = 0.87$) (**57**) and $[Zn^{II}Pc(EtS^-)_y(I^-)_{1-y}]_2 .(C_{60}^-)_2(PMDAE^+)_4(C_6H_4Cl_2)$ ($y = 0.5$) (**58**).[195]

3. As an example of a loose (framework) three-dimensional packing of $C_{60}^{-\bullet}$ anions, consider the structure of compound **37** described in Section IV.3 (see Fig. 9).[127] The neighbouring anions occupy the vertices of a trigonal prism. Cavities or channels filled with cations and solvent molecules are formed in the packing. Perhaps, framework structures of other types formed upon other patterns of superimposition of loose hexagonal layers may be discovered in the future.

4. Fulleride anions can form close-packed linear or zigzag chains with two neighbours for each anion. Structures of this type have been found in $(TDAE^{+\bullet})C_{60}^{-\bullet}$ (**1**) (see Fig. 6 *a*),[162] $(CoCp_2)^+(C_{60}^{-\bullet})CS_2$ (**5**) (see Fig. 7 *a*),[102] $\{K^+(THF)_5\}C_{60}^{-\bullet}(THF)_2$ (**68**) (see Fig. 15 *a*)[80] and in a series of ionic multicomponent complexes of fullerenes with metal porphyrins **52**–**55**.[186, 193]

5. If all distances between the centres of C_{60} anions are greater than 12 Å, this can be classified as an island structure with isolated anions; there are no direct van der Waals contacts between the anions. This type of packing is observed in compounds with bulky Ph_4P^+ (Refs 66, 153–155), PPN^+ (Ref. 157) and $Ru(bipy)_3^{2+}$ (Ref. 99) cations and in salts **32**–**34**, **69** containing fulleride anions with a charge of −2 or −3 and alkali metal cations, which coordinate THF, crown ether or cryptand molecules.[74–76, 79]

Table 7. Average [6,5]- and [6,6]-bond lengths for C_{60}, its complexes and salts from single-crystal X-ray diffraction data.

Compound	Charge on C_{60}	Length of the [6,5]-bond /Å	Length of the [6,6]-bond /Å	Ref.
C_{60}	0	1.455(8)	1.391(8)	238
$(BEDT\text{-}TTF)_2C_{60}$	0	1.452(1)	1.389(7)	239
$(FeCp_2)_2C_{60}$	0	1.450(5)	1.387(6)	240
$(NiCp_2^*)^+(C_{60}^{-\bullet})CS_2$ (**4**)	−1	1.449(3)	1.389(3)	106
$(TDAE^{+\bullet})C_{60}^{-\bullet}$ (**1**) (antiferromagnetic phase)	−1	1.453(5)	1.389(5)	170
$\{Ru^{2+}(bipy)_3\}(C_{60}^{2-})(PhCN)_2(PhMe)_2$ (**30**)	−2	1.449(5)	1.396(5)	99
$(Ba^{2+})(NH_3)_8(C_{60}^{2-})$ (**64**)	−2	1.447(5)	1.398(6)	121
$\{Mn^{2+}(NH_3)_9C_{60}^{2-}\}$ (**60**)	−2	1.446(5)	1.400(5)	117
$(Ni^{2+})(NH_3)_9(C_{60}^{2-})$ (**63**)	−2	1.446(5)	1.400(5)	118
$(Co^{2+})(NH_3)_9(C_{60}^{2-})$ (**61**)	−2	1.441(5)	1.393(6)	120
$\{K^+([2.2.2]cryptand)\}_2(C_{60}^{2-})(PhMe)_4$ (**32**)	−2	1.446(8)	1.391(6)	76
$(PPN)_2C_{60}$ (**24**)	−2	1.446(2)	1.399(2)	151
$\{Rb^+(benzo\text{-}18\text{-}crown\text{-}6)\}_3(C_{60}^{3-})(PhMe)(DMF)_{4.5}$ (**33**)	−3	1.443(5)	1.402(4)	75
$\{Rb^+(benzo\text{-}18\text{-}crown\text{-}6)\}_3(C_{60}^{3-})(PhMe)(DMF)_{4-x}(THF)_x$	−3	1.444(9)	1.397(9)	75
Rb_4C_{60}	−4	1.44(2)	1.42(2)	213

VII. Spectroscopy of ionic compounds of fullerenes

A large number of original works and reviews are devoted to spectroscopic investigations of ionic fullerene compounds.[20–22, 34, 37, 243–266] From spectroscopic data, the charge state of the fullerene and the formation of σ-bonded dimeric and polymeric structures can be elucidated.

1. Electronic spectroscopy

The UV/Vis spectrum of neutral C_{60} fullerene was considered in detail in a review.[37] As fullerene is reduced, its LUMO starts to be occupied, and intramolecular transitions from the fullerene LUMO to upper LUMO + 1 and LUMO + 2 become possible. As a consequence, additional absorption bands in the near-IR region appear in the spectra of fullerene anions. Each anion produces its own characteristic absorption bands: 940–950 and 1070–1080 nm for $C_{60}^{\bullet-}$; 840, 950–960 and 1320–1330 nm for C_{60}^{2-}; and 800, 870–880, 1000–1010 and 1380 nm for C_{60}^{3-} (Fig. 20).[115, 243] The spectrum of C_{60}^{4-} shows two principal bands at 730 and 1195 nm.[72] In the case of C_{70}, the bands recorded for anions in solutions were 1374 nm for $C_{70}^{\bullet-}$ (Fig. 21, spectrum *5*); 670 and 1182 nm for C_{70}^{2-}; and 670, 770 and 1170 nm for C_{70}^{3-} (Ref 243).

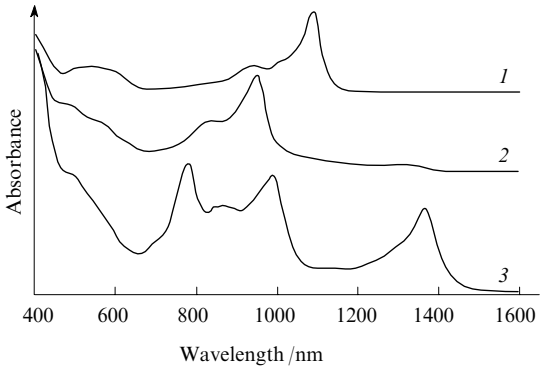


Figure 20. Optical absorption spectra in DMF solutions of the $C_{60}^{\bullet-}$ radical anion (Mg) (*1*), the C_{60}^{2-} dianion (Mg–KOH) (*2*) and the C_{60}^{3-} trianion (Zn–KOH) (*3*).[115] In parentheses, the reducing agents used are indicated.

After dimerization, the general features of the near-IR spectrum of the $C_{60}^{\bullet-}$ radical anion are retained (Fig. 21, spectrum *1*) but some distinctions appear. In the spectrum of the $(C_{60}^{-})_2$ dimer formed by two C–C bonds, the 905 and 1064 nm bands are markedly broadened and, apart from these two bands, a new weak band appears at 1330 nm (see Fig. 21, spectrum *3*). This band is missing from the spectrum of $C_{60}^{\bullet-}$ (see Fig. 21, spectrum *1*) and may be attributed to the charge transfer between C_{60}^{-} in the dimer. The complex $(DMETEP^{+})_2(C_{60}^{-})_2\{(Mn^{II}TPP)_2DMP\}.(C_6H_4Cl_2)_5$ ($DMETEP^{+}$, see Fig. 4) is still the only one compound in which the $(C_{60}^{-})_2$ dimer linked by one C–C bond exists at room temperature but its content is only 86%, since the complex also contains the $(C_{60}^{-})_2$ dimer linked by two C–C bonds (14%).[244] The spectrum of this complex, too, apart from the two principal absorption bands at 950 and 1070 nm contains an additional weak band at 1380 nm (see Fig. 21, spectrum *2*).

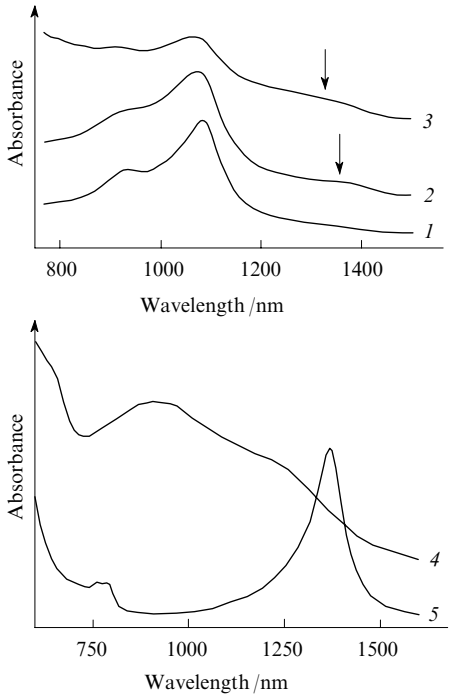


Figure 21. Optical absorption spectra of fullerene monomers and dimers in the visible and near-IR region at 293 K in KBr pellets (*1–4*) and in a $C_6H_4Cl_2$ solution (*5*).
(*1*) $C_{60}^{\bullet-}$ radical anion in complex **10**;[100] (*2*) $(C_{60}^{-})_2$ dimer linked by one C–C bond with impurity of $(C_{60}^{-})_2$ dimer with two C–C bonds (14%);[244] (*3*) $(C_{60}^{-})_2$ dimer linked by two C–C bonds in complex **50**;[188] (*4*) $(C_{70}^{-})_2$ dimer linked by one C–C bond in complex **13**;[101] (*5*) $C_{70}^{\bullet-}$ radical anion in the reduction of C_{70} by $Cr(C_6H_6)_2$.[101]

The monomeric radical anion, $C_{70}^{\bullet-}$, shows a near-IR absorption band at 1363–1386 nm (see Fig. 21, spectrum *5*). Dimerization induces pronounced changes in the initial spectrum; instead of one band, the spectrum of the $(C_{70}^{-})_2$ dimer exhibits two broad bands at 880 and 1240 nm (see Fig. 21, spectrum *4*). This type of spectrum is recorded for all ionic compounds containing $(C_{70}^{-})_2$ dimers. In the case of $(C_{70}^{-})_2$, it is difficult to find which of the two bands is the charge transfer band.

2. IR spectroscopy

The fullerene C_{60} is highly symmetric (I_h); therefore, out of the 46 normal vibrations characteristic of the C_{60} molecule, only four [$T_{1u}(1-4)$ modes with 527, 577, 1183 and 1429 cm^{-1} absorption bands, respectively] are IR-active, while ten are Raman-active. The transfer of electron density to the ground-state C_{60} molecule induces a shift of some absorption bands and a considerable increase in their integrated intensity. This is caused by occupancy of the t_{1u} orbital of fullerene and interaction of the T_{1u} vibrations with the virtual electron transitions from the t_{1u} orbital to the upper t_{1g} orbital.[245, 246] These effects are observed in both IR and Raman spectra; therefore, they are very convenient for the estimation of the charge state of fullerene in ionic compounds. Table 8 presents the positions of the four IR-active $T_{1u}(1-4)$ vibrations of C_{60} in ionic compounds with different charge states. Analysis of these data indicates that upon reduction of C_{60}, the band related to the

Table 8. Positions of absorption bands of the C_{60} $T_{1u}(1-4)$ vibrations (ν) in ionic compounds with monomeric anions.

Compound	Charge on C_{60}	ν/cm^{-1}				Ref.
		$T_{1u}(1)$	$T_{1u}(2)$	$T_{1u}(3)$	$T_{1u}(4)$	
C_{60}	0	526	576	1182	1429	20
TDAE·C_{60}	−1	514, 526	575	1182	1389	249
$(Ph_4P)_2C_{60}$ X (X = I, Br, Cl)	−1	527	576	1179	1394	250
$(CrCp^*_2)^+(C_{60}^{-\bullet})(C_6H_4Cl_2)_2$ (**10**)	−1	527	577	1181	1393	100
$(CoCp^*_2)^+_2(C_{60}^{2-})(C_6H_4Cl_2,PhCN)_2$ (**16**)	−2	520	574	1182	1369	179
K_3C_{60}	−3	–	572	–	1363	246
K_4C_{60}	−4	–	568	–	1350	246
K_6C_{60}	−6	467	564	1183	1341	246

$T_{1u}(4)$ vibration shifts to lower wavenumbers: from 1429 cm^{-1} in neutral C_{60} to 1340 cm^{-1} in salts of C_{60}^{6-}. The $T_{1u}(1)$ and $T_{1u}(2)$ vibration bands also shift upon the reduction of C_{60} but these shifts are much smaller than those in the case of the $T_{1u}(4)$ band (see Table 8). As C_{60} is reduced, the integrated intensity of the $T_{1u}(2)$ and $T_{1u}(4)$ bands considerably increases. This is caused by the fact that the oscillator strength of these modes increases nearly to the square of the negative charge on C_{60}.[246] The frequency of the Raman-active $A_{1g}(2)$ vibration corresponding to the 1467 cm^{-1} band in the parent C_{60} depends linearly on the charge state of the fullerene anion and shifts by approximately 6 cm^{-1} towards smaller wavenumbers upon addition of one electron to the C_{60} LUMO.[247,248]

The other 32 normal vibrations in C_{60} are not manifested in the spectra according to the symmetry selection rules; the observed modes of C_{60} are three- or five-fold degenerate.[20] As a result, the IR spectrum of C_{60} is highly sensitive to the change of the symmetry of the molecule. Any effects related to the formation of new C−C bonds upon dimerization or polymerization of fullerenes[20] result in the appearance of new absorption bands that were forbidden previously by the selection rules and also in the splitting of the existing bands into three or more lines. Indeed, the spectrum of the neutral $(C_{60})_2$ dimer, apart from the absorption bands of C_{60} (527, 575, 1186 and 1426 cm^{-1}), contains 420, 479, 549, 612, 709, 726, 769, 796 and 1462 cm^{-1} bands induced by the decrease in the symmetry of the fullerene cage.[220] Upon the formation of the negatively charged dimer, $(C_{60}^{-})_2$, with two exopolyhedral C−C bonds in complex **50**, the 1426 cm^{-1} absorption band shifts to smaller wavelengths and splits into three components at 1406, 1398 and 1388 cm^{-1} (Ref. 188). The band at 575 cm^{-1} is more intense than the band at 527 cm^{-1}; this is also characteristic of the $C_{60}^{-\bullet}$ radical anions.[246] Other absorption bands in the spectrum of compound **50** [188] (420, 482, 546, 606, 712, 796 and 1462 cm^{-1}) are located close to those in the spectrum of the neutral $(C_{60})_2$ dimer. The absorption spectrum of neutral C_{70} has 10 bands.[20] The formation of the $(C_{70}^{-})_2$ dimer linked by one C−C bond gives rise to numerous new bands at 494, 508, 530, 548, 556, 574, 628, 638, 668, 688, 713, 721, 800, 842, 901, 944, 1158, 1176, 1210, 1245, 1279, 1307, 1323, 1354, 1363, 1391, 1412, 1430, 1478, 1508 and 1560 cm^{-1} (Refs 163, 193, 218 and 219). These bands are suitable for the identification of $(C_{70}^{-})_2$ dimers in ionic complexes.

3. EPR spectroscopy

EPR spectroscopy is a convenient method for investigation of ionic compounds of fullerenes. The parent fullerenes are diamagnetic; therefore, samples of pure fullerenes exhibit only weak, narrow residual signals due to impurities.[251,252] When anions are formed, fullerene acquire unpaired electrons, which is detected by EPR spectroscopy.

As discussed above, the $C_{60}^{-\bullet}$ radical anion has a doublet ground state ($S = 1/2$) and the corresponding EPR signal has a g-factor ranging from 1.9979 to 1.9992 (Table 9), which is much smaller than the g-factor for free electron (2.0023). The EPR signals of $C_{60}^{-\bullet}$ are wide at room temperature ($\Delta H = 3-6$ mL) but as temperature decreases, these lines considerably narrow down: to 0.5–1 mT at 80 K (see Table 9). Thus, the EPR spectra of $C_{60}^{-\bullet}$ are characterized by low g-factors and great linewidth under ambient conditions.

The small g-factors found for the $C_{60}^{-\bullet}$ radical anions are attributed to spin–orbit coupling effects of the unpaired electrons in the degenerate ground state.[253] Higher fullerenes have lower symmetry, they have no degenerate LUMO, and, hence, the g-factors of EPR signals of the radical anions of these fullerenes are similar to the value characteristic of free electron (see Table 9). The addition of addends to the C_{60} carbon cage also substantially reduces the fullerene symmetry and removes the orbital degeneracy; therefore, the g-factors of the EPR signals of radical anions derived from fullerenes move towards 2.0023. For instance, the g-factor of $C_{60}(CN)_2^{-\bullet}$ is 1.9997–1.9998 (see Table 9), while for most of radical anions of fullerene derivatives generated in solutions the g-factors are most often >2.0000.[254–256]

The half-width of the EPR signal of $C_{60}^{-\bullet}$ may vary from 3 to 8 mT at room temperature depending on the cation; therefore, it was assumed in a review[96] that it is mainly determined by the effect of spin–lattice relaxation. However, the half-width of the EPR signal appears to depend considerably on some other factors such as the presence of low-lying excited states[257,258] and pseudorotations of $C_{60}^{-\bullet}$ (Refs 257 and 259) related to a decrease in the symmetry of $C_{60}^{-\bullet}$ caused by the Jahn–Teller effect. In the former case, the decrease in the symmetry induces splitting of the three-fold degenerate LUMO of fullerene into (at least) two levels: the occupied ground level ^{2}A and the closely located level ^{2}E. The presence of the low-lying excited level should induce broadening of the EPR signal due to the Orbach process;[257] it is important that the energy difference (ΔE)

Table 9. Values of *g*-factor and line half-width (ΔH) for the EPR signal of fullerene anions in ionic compounds.

Compound	Charge on C_{60}	*g*-Factor, signal assignment	T/K [a]	ΔH/mT [a]	Ref.
$(PPN^+)(C_{60}^{-\bullet})PhCl$ (**23**)	−1	1.9992	rt (77)	3.5 (0.5)	156
		2.0007	$T > 50$	0.1 – 0.2	156
$(Ph_4P^+)_2(C_{60}^{-\bullet})I^-$ (**20**)	−1	2.001	rt (113)	5.0 (1.4)	66
$Na^+(C_{60}^{-\bullet})(THF)_5$ (**70**)	−1	1.999	rt (120)	3.5(0.8)	81
$(Na^+)_{0.4}(C_{60}^-)(THF)_{2.2}$ (**72**)	−0.4	1.999	rt	3.0	85
$\{Co^{2+}(DMF)_{3.3}\}(C_{60}^{-\bullet})_2$ (**74**)	−1	1.9951	rt	5.65	196
		1.9850	6	35.65	196
$(TDAE^+)(C_{60}^{-\bullet})$ (**1**)	−1	2.0008, $Ct^+ + C_{60}^{-\bullet}$	rt	2.2	171
		2.0017 – 2.0030	< 16 [b]	3.0	171
$\{Cr^I(C_6H_6)_2^{+\bullet}\}(C_{60}^{-\bullet})C_6H_4Cl_2$ (**11**)	−1	1.9913, $Ct^+ + C_{60}^{-\bullet}$	rt, monomer	–	101
		1.986, Ct^+	T < 250 K, dimer	–	101
$\{Cr^I(PhMe)_2^{+\bullet}\}C_{60}^{-\bullet}$ (**7**)	−1	1.9915, $Ct^+ + C_{60}^{-\bullet}$	rt, monomer	–	105
		1.9868, Ct^+	T < 250 K, dimer	–	105
$(TDAE^{+\bullet})(C_{70}^-)(C_6H_4Cl_2)$	−1	2.0032, Ct^+	rt, dimer	0.46	163
$(Ph_4P^+)_2(C_{70}^{-\bullet})I^-$ (**21**)	−1	2.047	rt (4.2)	60(0.15)	67
$(TDAE^+)(C_{84}, C_{90}, C_{96}^-)$	−1	2.0020 – 2.0022	rt	0.185 – 0.240	172
$(CoCp_2)^+\{C_{60}(CN)_2^{-\bullet}\}CS_2$	−1	1.9998	rt	0.21	102
$K^+\{C_{60}(CN)_2^{-\bullet}\}(THF)_x$	−1	1.9997	rt	0.28	55
$(PPN^+)_2(C_{60}^{2-})$ (**24**)	−2	2.0010	77	0.1 – 0.3	70
		1.999 – 2.000	T < 100	$2D$ = 1.9, triplet [c]	70
			30 < T < 155	$2D$ = 2.9, triplet [c]	70
$(CoCp_2^*)_2^+(C_{60}^{2-})(C_6H_4Cl_2, PhCN)_2$ (**16**)	−2	2.0006 [d]	T > 140	5.6	179
		2.0009 [e]	4 – 140	0.5	179
		2.0008 [f]	4 – 295	0.2	179
$\{K^+(18\text{-crown-6})\}_3(C_{60}^{3-})(PhMe)_2$ (**34**)	−3	2.001	rt	4.1	74
		2.000	rt	0.8	74
$(C_{60}^{+\bullet})(CB_{11}H_6Br_6^-)$	1	2.002	5	0.8	252
$(C_{76}^{+\bullet})(CB_{11}H_6Br_6^-)$	1	2.0030 (solution)	rt	0.05	15
		2.0042 (solid)	rt	0.27	15

[a] The values in parentheses refer to the same signal at lower temperature; [b] EPR signal appears after the compound transforms to the ferromagnetic state; [c] D is the zero-field splitting parameter; [d] at rt corresponds to a 6% occupancy of the excited triplet state; [e] integrated intensity 0.3% of the overall content of C_{60}; [f] integrated intensity 0.1% of the overall content of C_{60}.

between the two levels be rather small (about 150 cm^{-1}). Indeed, the theoretical estimates and experimental data give similar values for ΔE between the ground and excited levels in $C_{60}^{-\bullet}$, namely, about 150 – 240 cm^{-1} both in solution and in the solid state.[257, 259, 260] The calculations of the electronic structure of the ordered $C_{60}^{-\bullet}$ radical anion in the salt $\{Co(dppe)_2^+\}C_{60}^{-\bullet}(C_6H_4Cl_2)_2$ (**31**) also demonstrated that the gap between the ground and excited levels is only 180 cm^{-1} (Ref. 183). Note that other effects resulting in the distortion of the fullerene cage and, correspondingly, in the splitting of the $C_{60}^{-\bullet}$ LUMO, such as asymmetric environment, can also induce broadening of the EPR signals.[261] For compounds with radical anions of higher fullerenes and fullerene derivatives with low symmetry, narrow EPR signals with half-width not exceeding 0.3 mT are formed most often (see Table 9). An exception is the salt $(Ph_4P^+)_2(C_{70}^{-\bullet})I^-$, which gives rise to a broad EPR signal at room temperature (ΔH = 60 mT).[67]

The Jahn – Teller effect may be either dynamic or static on the EPR time scale.[259] At room temperature, dynamic effect is observed with fast transition from one static Jahn – Teller configuration to the other one (so-called pseudo-rotation). The frequency of this pseudo-rotation was estimated as $\sim 10^{12}$ Hz from EPR data.[259] As temperature decreases, the pseudo-rotation is retarded, the EPR signal narrows down, and transition to the static Jahn – Teller effect occurs. In $(Ph_4P^+)(C_{60}^{-\bullet})(Ph_4PCl)_2$, this transition takes place when the temperature has been lowered to 70 K,[257] being accompanied by sharp narrowing of the EPR signal; on further decrease in temperature, the linewidth barely changes.

The static Jahn – Teller effect leads to ellipsoidal distortion of the $C_{60}^{-\bullet}$ radical anion in which the negative charge should be delocalized around the equator, and consequently the isotropic EPR signal is converted to anisotropic signal. Single crystal studies demonstrated that the EPR signal anisotropy can be observed for the crystals of ionic fullerene compounds at low temperatures. The principal axes of the *g*-tensor for $C_{60}^{-\bullet}$ in $(Ph_4P^+)_2(C_{60}^{-\bullet})I^-$ are as follows: $g_x = g_y = 1.9970$, $g_z = 1.9998$ with a averaged *g*-factor of 1.9979 (4 K), whereas for $C_{70}^{-\bullet}$ in $(Ph_4P^+)_2(C_{70}^{-\bullet})I^-$, $g_x = g_y = 1.9998$, $g_z = 2.0150$ (along the principal axis of the molecule) with a averaged *g*-factor of 2.0047 (4 K).[67]

In the early works dealing with ionic compounds of fullerenes, narrow signals with *g*-factors of 2.0000 to 2.0031 and ΔH = 0.1 – 0.2 mT were often observed in the EPR spectra apart from the broad signals due to the fullerene radical anions. These signals are easily saturated unlike the signals of $C_{60}^{-\bullet}$; therefore, they are completely suppressed at high microwave power. This difference between the behaviours allows one to assign the broad and the narrow signals to independent spins. In some works, narrow signals were

attributed to thermal population of an higher-lying excited level that appeared upon splitting of the C_{60} LUMO into two levels due to decrease in the molecular symmetry (*e.g.*, due to the Jahn–Teller effect).[63, 156, 262] Subsequently the narrow EPR signals started to be attributed to the presence of $C_{120}O$ dimer impurity in the fullerene sample, which appeared upon the contact of fullerene with oxygen. During the formation of the ionic compound, the $C_{120}O$ impurity is also reduced to the $C_{120}O^{-\bullet}$ radical anion, which is responsible for a narrow EPR signal with a *g*-factor of 2.0012 and $\Delta H = 0.2$ mT.[207] Being engaged in the synthesis of ionic compounds, we also found that the narrow EPR signals appear upon the oxidation of $C_{60}^{-\bullet}$ with air oxygen in solution. Since solutions of $C_{60}^{-\bullet}$ are highly sensitive to oxygen, the presence of even traces of oxygen during the preparation of ionic compounds can result in narrow EPR signals ($g = 2.0000$, $\Delta H = 0.15$ mT at 77 K).[115]

Despite the presence of simultaneously two spins in the ionic compound (on the fullerene anion and on the cation), the EPR spectrum most often contains only one signal with a *g*-factor intermediate between the *g*-factors of the isolated ions (see Table 9). This is caused by the fast exchange interaction between the paramagnetic ions. For example, in $(TDAE^{+})(C_{60}^{-\bullet})$ (**1**), the *g*-factor of the EPR signal is 2.0008, which is an intermediate value between the *g*-factors of 2.0035 and 1.996–1.999, which are inherent in $TDAE^{+\bullet}$ and $C_{60}^{-\bullet}$, respectively.[171] The complexes $\{Cr^{I}(PhMe)_2^{+\bullet}\}C_{60}^{-\bullet}$ (**7**) and $\{Cr^{I}(C_6H_6)_2^{+\bullet}\}C_{60}^{-\bullet}(C_6H_4Cl_2)$ (**11**) at room temperature exhibit one EPR signal with a *g*-factor of 1.991. This value is also intermediate between the *g*-factors of 1.986 and 1.996–1.999, which are observed for individual bis(arene)chromium cations and $C_{60}^{-\bullet}$ ions respectively. The formation of the diamagnetic dimer $(C_{60}^{-})_2$ in compounds **7** and **11** leads to a decrease in the signal *g*-factor from 1.991 to 1.986.[105, 101] The latter value coincides with the *g*-factor of the EPR signal characteristic of an isolated bis(arene)-chromium cation.[263]

The C_{60}^{3-} trianions have a doublet ground state ($S = 1/2$) and demonstrate a rather broad signal at room temperature; for example, the EPR signal of $\{K^{+}(18\text{-crown-6})\}_3.C_{60}^{3-}(PhMe)_2$ (**30**) has $g = 2.001$ and $\Delta H = 4.1$ mT. Against the background of a broad signal, a narrower weak signal is recorded, probably, related to oxidation.[74] The *g*-factors for known compounds of C_{60}^{3-} are in the range of 2.0012–2.0017 and $\Delta H = 1.0–4.0$ mT.[73–75]

The EPR spectra of dianions exhibit weak narrow signals. In some cases, even a weaker triplet signal is observed against the background of the central signal (see Table 9).[70] No quantitative estimate of the intensities of these signals was carried out, and, most likely, they are due to impurities. The EPR spectrum of $(CoCp_2^{*})_2^{+}(C_{60}^{2-})(C_6H_4Cl_2,PhCN)_2$ (**16**) at $T < 140$ K exhibits two narrow EPR signals with $g = 2.0009$ ($\Delta H = 0.5$ mT) and $g = 2.0008$ ($\Delta H = 0.2$ mT). The intensities of these signals correspond to only 0.4% of the total content of C_{60}. A new broad EPR signal appears for complex **16** at $T > 140$ K; its intensity increases with temperature. This signal can be assigned to thermal population of the higher-lying triplet level. Like the signal of C_{60} mono- and trianions, this signal has a rather large half-width ($\Delta H = 5.6$ mT at room temperature) but has no triplet features. Perhaps, they cannot be observed at high temperatures (140–295K) due to various dynamic effects that average the zero-field splitting. The ΔE gap between the singlet and triplet levels for C_{60}^{2-} in complex **16** was estimated to be 730 ± 10 cm^{-1}, while the population of the triplet level at room temperature reaches 6%.[179]

The $C_{60}^{+\bullet}$ radical cations show the EPR signals with *g*-factors similar to that for free electron (2.002). In still the only radical cation compound of higher fullerene, $(C_{76}^{+\bullet})(CB_{11}H_6Br_6^{-})$, containing monomeric $C_{76}^{+\bullet}$ cation, a narrow signal with $g = 2.0042$ is present (see Table 9).

4. ^{13}C NMR spectroscopy

The ^{13}C NMR spectrum of crystalline C_{60} at room temperature contains a narrow singlet at 143 ppm.[264] Upon the formation of fullerene anions, C_{60}^{n-} ($n = 1–6$), the ^{13}C NMR signal shifts downfield. There is no correlation between the charge on the anion and the shift; therefore, determination of the charge state of fullerene from ^{13}C NMR data is hardly possible. For the $C_{60}^{-\bullet}$ radical anion and C_{60}^{3-} trianion, the ^{13}C NMR signals occur at 185–188 and 180–195 ppm, respectively.[77, 78, 81, 105, 116, 262, 265] For the C_{60}^{2-} dianion, the position of the ^{13}C NMR signal at room temperature (180–184 ppm)[78, 116, 266] is similar to those for C_{60} mono- and trianion, but unlike these anions, this signal slightly shifts upfield as the temperature decreases.[78] This may be due to the diamagnetic ground state of C_{60}^{2-} at low temperatures and thermal populating of the triplet excited level upon temperature rise. The diamagnetic C_{60}^{6-} hexaanion is responsible for the ^{13}C NMR signal at 156 ppm.[265] It is of interest that dimerization of $C_{60}^{-\bullet}$ in the complex $\{Cr^{I}(PhMe)_2^{+\bullet}\}C_{60}^{-\bullet}$ (**7**) induces the shift of the signal from 185 ppm, which is a typical position of the $C_{60}^{-\bullet}$ signal, to 146 ppm.[98] This may be due to the disappearance of the paramagnetic effect upon the formation of diamagnetic $(C_{60}^{-})_2$ dimers. Thus, the paramagnetism of $C_{60}^{-\bullet}$ has a crucial effect on the shift of the ^{13}C NMR signal.

VIII. Conclusion

Currently, a variety of approaches have been proposed for the synthesis of ionic compounds of fullerenes in solutions; the methods for the preparation of single crystals have been developed, a large number of such compounds have been prepared and their structures and properties have been studied. Now we will list the most promising, from our standpoint, lines of research in this area.

Ionic compounds of fullerenes can show ferromagnetic behaviour. The compound $TDAE \cdot C_{60}$ (**1**) does not contain metal atoms and can be considered as a purely organic magnet, which has a record-breaking ferromagnetic transition temperature among organic materials. The preparation of novel ionic magnetic compounds of fullerenes is faced with certain problems related to high chemical reactivity of their radical anions. For example, $C_{60}^{-\bullet}$ readily forms addition products with some amines, while radical anions of higher fullerenes starting with c C_{70} form diamagnetic dimers linked by one C–C bond. Nevertheless, the preparation of magnetic compounds with fullerene derivatives gives hope for further development and success in this field.

Peculiar magnetic properties are encountered among the ionic compounds of fullerenes with metallocenes, as most of metallocene cations are paramagnetic and can undergo exchange interactions with fullerene radical anions. However, in most of the obtained complexes with metallocenes, fullerene radical anions dimerize. The phases containing dimers are usually paramagnetic or diamagnetic. Mainte-

nance of radical anions in ionic compounds in the monomeric state down to low temperatures is possible only where there is steric hindrance for dimerization. For example, CS_2 solvent molecules are inserted between the fullerene anions in the compounds $NiCp^*_2C_{60}\cdot CS_2$ (**4**)[106] and $CoCp_2C_{60}\cdot CS_2$ (**5**);[102] this prevents them from dimerization, despite the presence of short contacts between the fullerene cages. The introduction of molecules producing steric restrictions for dimerization would be helpful for creating new magnetic compounds of fullerenes.

The manufacture of new, highly conductive compounds based on fullerenes requires the design of structures comprising close-packed one-, two- and three-dimensional aggregates of $C_{60}^{-\bullet}$ and C_{60}^{3-} anions. It is necessary to avoid dimerization, because the phases containing dimers cannot have high conductivity. Several approaches can be proposed. By introducing a neutral component of a definite shape and size into the ionic complex, it is possible to separate the fullerene spheres and prevent them from dimerization, while the short van der Waals contacts between them are maintained. This approach is implemented in the complex $(MDABCO^+)C_{60}^{-\bullet}\cdot TPC$ (**80**), which is actually a quasi-2D metal down to 2 K.[147] Probably, the dimerization problem can be solved by preparing ionic compounds with the C_{60}^{3-} trianions because the pronounced repulsion of negative charges will, most likely, make dimers of trianions unstable. The exopolyhedral C–C bond in the $(C_{60}^{-})_2$ dimer is formed involving electrons of each of the $C_{60}^{-\bullet}$ anions. With partial charge transfer ($\delta \leqslant 0.5$), the dimeric state would be unstable; these compounds may be stable against dimerization and may show high conductivity. For example, no dimerization occurs in $(Na^+)_x(THF)_yC_{60}^{x-}$ ($x \approx 0.4$, $y \approx 2.2$) (**72**), despite the close packing of fullerene anions, and this compound has metallic properties.[84,85]

Previously, most of conducting and superconducting compounds of fullerenes were obtained by doping of fullerenes with alkali and alkaline earth metals and lanthanides.[14,28] However, the potential of preparing new M_xC_{60} products by doping is almost exhausted. Now a topical task is to prepare organic molecular metals based on C_{60} and higher fullerenes by direct synthesis from solution, in particular as crystals. Certain progress has been achieved along this route and a number of highly conductive phases, including those with metallic conductivity, have been obtained (compounds **38**, **72**, **73**, **80**).[84–86,116,147] It is noteworthy that all of these compounds have layered structures with close hexagonal packing of fullerene anions in the layer, *i.e.*, this packing is optimal for high electrical conductivity. Several compounds were obtained in which high conductivity is combined with magnetic interactions between the spins (complexes **74**–**76**) but the structures of these compounds have not yet been determined.[196] The synthesis of novel layered ionic derivatives may extend the range of highly conductive compounds (organic metals) based on fullerenes. To this end, in the case of close packing of fulleride anions, it is necessary to prevent dimerization by means of steric factors or to obtain compounds with partial charge transfer. Perhaps, salts with organic or organometallic cations may have other types of packing of fulleride anions that would also provide metallic behaviour.

The dimerization of fullerene anions interfere with the production of functional materials with conducting and magnetic properties based on them. Nevertheless, now it is already clear that some dimeric and polymeric fullerene anions retain the unpaired spins, and may exhibit interesting magnetic and conducting behaviour. The $(C_{60}^{-})_2$ dimer linked by two C–C bonds has triplet state at room temperature;[188–190] some polymers $(C_{60}^{-})_n$, $(C_{60}^{3-})_n$, $(C_{60}^{4-})_n$ retain the spins after polymerization and exhibit metallic properties and strong magnetic correlations.[223–225,227,233] These conducting fullerene polymers refer to highly correlated metals with a narrow conduction band and pronounced repulsion between the electrons in it. Even minor changes in the structure and orientation of the polymeric chains can lead to considerable changes of the physical properties of these polymers; in some cases, properties such as superconductivity may appear. For the synthesis of new fullerene polymers, it appears highly promising to study the polymerization of fulleride anions in ionic compounds with organic and organometallic donors at elevated pressure. It is demonstrated in the review that the ionic compounds of fullerenes possess a large diversity of anion packing (one-, two- and three-dimensional aggregates), and, hence, new types of fullerene polymers of various dimensions can be prepared in these compounds at elevated pressure. These elevated-pressure studies can be performed directly on single crystals of ionic compounds.

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