Reviews

Ionic fullerene compounds containing negatively charged dimers and coordinatively bound anions

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The review summarizes the results of investigations of ionic fullerene compounds containing negatively charged dimers and fullerene anions coordinated to metalloporphyrins. Fullerene radical anions were found to form diamagnetic singly bonded $(C_{60}^{-})_2$ and $(C_{70}^{-})_2$ dimers. Dimerization is reversible and leads to paramagnetic—diamagnetic phase transitions or a decrease in the magnetic moment of the complexes. The temperature, at which dissociation of the $(C_{60}^{-})_2$ dimers begins, varies from 140 to 320 K; the corresponding temperature for the $(C_{70}^{-})_2$ dimers varies from 260 to 360 K and higher. We prepared the first doubly bonded $(C_{60}^{-})_2$ dimer. At 300 K, this dimer exists as a biradical. The fullerene radical anions form Co–C coordination bonds with cobalt(11) porphyrinates. The resulting anions are diamagnetic. In some cases, Co–C coordination bonds undergo reversible dissociation, resulting in magnetic transitions from the diamagnetic to the paramagnetic state.

Key words: C_{60} and C_{70} fullerenes, donor-acceptor complexes, metallocenes, porphyrins, dimerization, coordination, crystal structure, magnetic properties, ESR spectroscopy, IR and near-IR spectra.

The discovery of a new allotrope of carbon,¹ viz., fullerene, resulted in the appearance of a unique threedimensional π acceptor. A large number of donor-acceptor compounds based on fullerenes both in the neutral and ionic ground state have been synthesized.^{2–5} Neutral compounds are of interest due to their photophysical properties.^{6,7} Ionic compounds containing fullerene radical anions C₆₀^{•n-} (n = 1 or 3) exhibit metallic conductivity, superconductivity, and ferromagnetism.^{2,5,8,9} Fullerene radical anions can exist either in the monomeric state or form dimers, polymers, or coordination bonds with organometallic donors.^{4,10} These processes give rise to a wide diversity of structures and properties of ionic fullerene compounds. An understanding and the prediction of such processes are of significance for the synthesis of the certain types of fullerene structures with desired physical

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 3, pp. 361-381, March, 2007.

1066-5285/07/5603-0371 © 2007 Springer Science+Business Media, Inc.

properties, which are of importance for the design of new fullerenes based on functional materials.

Linear $(C_{60}^{-})_n$ polymers, in which each C_{60}^{-} anion is linked to the adjacent anions by four C-C bonds (Fig. 1, *a*), were found for the first time in the $M \cdot C_{60}$ compounds (M = K, Rb, or Cs). The $K \cdot C_{60}$ compound behaves as a three-dimensional metal up to 4 K, whereas the compounds with M = Rb or Cs are quasi-one-dimensional metals, which undergo the metal-insulator phase transition at $T \le 50$ and 40 K, respectively.^{11–13} Under high pressure, the Na₂Rb \cdot C₆₀ and Li₃Cs \cdot C₆₀ compounds form linear $(C_{60}^{3-})_n$ polymers, in which each trianion is linked to the adjacent trianions by two C-C bonds. The starting compounds containing monomeric trianions are superconductors, and polymerization leads to the disappearance of superconductivity, whereas the metallic properties are retained.^{16,17} In the salts of C_{70} with metal cations, viz., $\{(Ba^{2+}) \cdot (NH_3)_7\} \cdot (C_{70}^{2-}) \cdot (NH_3)_9$, $\{(Sr^{2+}) \cdot (NH_3)_8\} \cdot (C_{70}^{2-}) \cdot (NH_3)_3$, and $\{(Sr^{2+}) \cdot (NH_3)_8\}_3$. • $(C_{70}^{3-})_2 \cdot (NH_3)_{19}$, which were prepared by diffusion in liquid ammonia, polymers consisting of C_{70}^{2-} dianions



Fig. 1. Linear $(C_{60}^{-})_x$ polymer in the $M \cdot C_{60}$ compounds $(M = K, Rb, \text{ or } Cs) (a)^{11-13}$; the $(C_{70}^{2-})_x$ polymer in the $\{(Sr^{2+}) \cdot (NH_3)_8\} \cdot (C_{70}^{2-}) \cdot (NH_3)_3$ salt $(b)^{14}$; and the two-dimensional $(C_{60}^{4-})_x$ polymer in the Na₄C₆₀ compound (c).¹⁵

(see Fig. 1, *b*) and C_{70}^{3-} trianions are formed.^{14,18,19} In the Na₄·C₆₀ compound, the C₆₀⁴⁻ tetraanions form two-dimensional polymers, each tetraanion being involved in four new C–C bonds (see Fig. 1, *c*) with four other tetraanions.¹⁵

The hypothesis about the existence of singly bonded $(C_{60}^{-})_2$ dimers has been made in the analysis of X-ray powder diffraction data for the metastable phases $M \cdot C_{60}$ (M = K, Rb, or Cs). These singly bonded dimers are diamagnetic (Fig. 2, *a*).^{20–23} Dimers of neutral fullerenes were documented. Fullerene C_{60} forms the doubly bonded $(C_{60})_2$ dimer.^{24,25} In the neutral azafullerene dimer $(C_{59}N)_2$, the monomers are linked to each other by only one C–C bond, and this dimer is isoelectronic with $(C_{60}^{-})_2$.²⁶

Many ionic fullerene compounds containing organic or organometallic donors and cations (Fig. 3) involve monomeric radical anions. These are TDAE $\cdot C_{60}$,⁹ Cp₂Co $\cdot C_{60} \cdot CS_2$,²⁷ Cp*₂Ni $\cdot C_{60} \cdot CS_2$,²⁸ Cr^{III}TPP $\cdot C_{60} \cdot (THF)_3$,²⁹ and (Cp*₂Co)₂ $\cdot C_{60} \cdot (PhCN, C_6H_4Cl_2-o)_2$,³⁰ salts of C_{60}^{n-} (n = 1, 2, or 3) and C_{70}^{-} with PPN⁺ (PPN is bis(triphenylphosphoranylidene)ammonium), Ph_4P^+ , or Ph_4As^+ cations, 31-35 and salts of C_{60}^{n-} (n = 2 or 3) with alkali metal cations 36-38 or some other cations.³⁹ The properties of these compounds were discussed in the review.³⁹ Rather recently, polymeric and dimeric structures formed by fullerene anions were found in these compounds. In the $Cr(C_6H_5Me)_2 \cdot C_{60} \cdot CS_2$ compound, the C_{60}^{-} anions are apparently linked to each other by two C-C bonds to form a linear polymer. However, the structure of this polymer cannot be satisfactorily characterized because of a disorder of the C_{60}^{-} anions.⁴⁰ In the ferromagnetic TDAE $\cdot C_{60}$ salt, the $C_{60}^{\cdot -}$ radical anions undergo polymerization under a pressure of 7 kbar; the resulting polymeric phase is stable under atmospheric pressure and undergoes depolymerization only upon heating above 520 K.41,42

The reversible phase transition associated with dimerization of C_{60} . was observed for the first time in the $Cr(C_6H_5Me)_2 \cdot C_{60}$ compound at 250 K (X-ray powder diffraction data). A model of the molecular structure of the $(C_{60}^{-})_2$ dimer was proposed and the C–C bond length between the C_{60}^{-} anions in the dimer was estimated (1.55 Å).43,44 A complete X-ray diffraction study of the molecular structure of the singly bonded $(C_{60})_2$ dimer (σ dimer, see Fig. 2, *a*) became possible after the preparation of single crystals of $Cp_2^*Cr \cdot C_{60} \cdot (C_6H_4Cl_2)_2$ (Cp*₂Cr, see Fig. 3).⁴⁵ Similar dimers were found in some other ionic complexes of C₆₀ with Cp₂Co,⁴⁶ $Cr(C_{6}H_{6})_{2}$, ^{46,47} and $Cr(Ph-Ph)_{2}$ ⁴⁸ and the $(Cs)_{2}$. $\cdot (C_{60})_{2} \cdot CTV \cdot (DMF)_{6}$ ⁴⁹ and $Cr(C_{6}H_{6})_{2} \cdot C_{60}$. • $[Pd(dbdtc)_2]_{0.5}$ complexes.⁵⁰ The ESR and ¹³C NMR spectroscopic studies demonstrated that the C_{60} · - radical anion in the structure of $Cr(C_6H_3Me_3)_2 \cdot C_{60}$ also, apparently, undergoes dimerization. However, a reversible



Fig. 2. Molecular structures of dimers and coordinatively bound anions: the $(C_{60}^{-})_2 \sigma$ dimer (*a*); the doubly bonded $(C_{60}^{-})_2$ dimer (*b*); the $(C_{70}^{-})_2 \sigma$ dimer (*c*); the coordinatively bound { $Co^{II}TPP \cdot (C_{60}^{-})$ } anion (*d*), the coordinatively bound { $(Co^{II}OEP \cdot (C_{60}^{-}))$ } anion (*e*), and the coordinatively bound { $Co^{II}TPP \cdot (C_{60}(CN)_2^{-})$ } anion (*f*) (OEP is octaethylporphyrinate and TPP is tetraphenylporphyrinate).

stepwise decrease in the magnetic moment attendant on dimerization was not observed. Presumably, dimerization in this complex occurs not as a first-order phase transition (like in other known compounds) but as a higher-order phase transition.⁵¹ The C_{60} - radical anions also form unusual negatively charged doubly bonded (C_{60} -)₂ dimers (π dimers; see Fig. 2, *b*). The electronic structures of these dimers are substantially different from those of σ dimers.⁵² In some compounds, doubly bonded dimers coexist with σ dimers.⁵³

The C_{70} [•] radical anions also prone to form singly bonded diamagnetic $(C_{70}^{-})_2$ dimers. The molecular structure of such dimers (see Fig. 2, *c*) has been established for the first time in the X-ray diffraction study of crystals of $(Cs)_2 \cdot (C_{70})_2 \cdot \text{CTV} \cdot (\text{DMF})_7 \cdot (C_6H_6)_{0.75}$ (CTV, see Fig. 3).⁵⁴ Analogous dimers are formed (magnetic measurement data) in complexes of C_{70} with $\text{Cr}(C_6H_6)_2$,^{46,55} Cp_2Co ,⁴⁶ Cp_2^*Cr ,⁵⁵ Cp_2^*Ni ⁵⁵ (see Fig. 3), and Cs.⁴⁶ In the structure of TDAE $\cdot C_{70} \cdot C_6H_5$ Me, the presence of $(C_{70}^{-})_2$ was proved by single-crystal X-ray diffraction.⁵⁶ Several ionic complexes of dicyanofullerene $C_{60}(CN)_2$ were characterized.^{57,58} Dimerization of $C_{60}(CN)_2^{-}$ was proved at least in the complex with bis(benzene)chromium $Cr(C_6H_6)_2$.⁵⁸

Metal octaethyl- and tetraphenylporphyrinates (see Fig. 3) form neutral complexes with fullerenes, their derivatives, and endometallofullerenes.^{59–71} In these complexes (particularly, with metalloporphyrins containing $M = Co^{II}$, Fe^{II}, or Fe^{III}),^{64,66–68} there are rather strong M...C_{Ful} interactions. The M...C distances are 2.55–2.70 Å, which are smaller than the sum of the van der Waals radii of the M and C atoms (~3.1 Å) but are substantially longer than the Co–C coordination bonds in alkylcobalamines (1.99–2.03 Å).⁷² In these complexes, interactions between metalloporphyrins and neutral fullerenes can be described as secondary bonding.⁶³ The bonds between the fullerene radical anions and cobalt(II) porphyrinates are stronger than those with neu-



TDAE is tetrakis(dimethylamino)ethylene, DMP⁺ is the N,N -dimethylpyrazolium cation, CTV is cyclotriveratrylene, DMETEP⁺ is the N -(ethylthioethyl)-N,N -dimethylpiperazinium cation, MP⁺ is the N-methylpyridinium cation, Pd(dbdtc)₂ is palladium(II) dibenzyldithiocarbamate, and

MDABCO⁺ is the *N*-methyldiazabicyclooctane (4-aza-1-methylazoniabicyclo[2.2.2]octane) cation.

Fig. 3. Molecular structures of the donors and cations used for the synthesis of ionic fullerene compounds.

tral fullerenes, and these radical anions form coordinatively bound anions (see Fig. 2, d-f).⁷³⁻⁷⁶ The latter can be stable up to room temperature^{75,76} or undergo dissociation upon heating. It is also possible to synthesize complexes containing uncoordinated cobalt(II) porphyrinates and fullerene anions^{*}.⁷⁷

The present review summarizes the results of investigations of ionic complexes and salts of fullerenes containing the negatively charged $(C_{60}^{-})_2$ and $(C_{70}^{-})_2$ dimers and coordinatively bound fullerene anions with cobalt(II) porphyrinates, which were synthesized by our research group in the last four years. The structural aspects of dimerization and coordination and the influence of various factors on stability of the resulting anionic species are discussed in detail. The magnetic and optical properties of ionic fullerene complexes and reversible changes in these properties as a result of the formation of dimers and coordinatively bound anions are considered.

1. Synthesis of complexes

Depending on the oxidation potential of the donor component (DC), fullerenes can form both ionic $(DC^{\delta+})(C_{60}^{\delta-})$ (charge transfer is close to unity, $\delta \sim 1$) and neutral $(DC^{\prime\delta+})(C_{60}^{\delta-})$ (charge transfer is close to

zero, $\delta \sim 0$ complexes. Partial charge transfer ($0 < \delta < 1$) is rarely observed in fullerene compounds.⁷⁸ Fullerenes behave as rather weak acceptors ($E^{0/-} = -0.44$ (C₆₀) and $-0.41 \text{ V} (C_{70})$.⁷⁹ Hence, the formation of ionic compounds would be expected only in the case of strong donors (DC), which are oxidized at a potential more negative than -0.5 V. These are Cp*₂Cr ($E^{+/0} = -1.04$ V),⁸⁰ Cr(C₆H₆)₂ ($E^{+/0} = -0.72$ V),⁸¹ TDAE ($E^{+/0} = -0.75$ V),⁸² and Cp₂Co ($E^{+/0} = -0.91$ V)⁸⁰ (all potentials were determined relative to a saturated calomel electrode). Ionic compounds can be synthesized in solution by direct reduction of fullerenes with strong donors (DC) or by cation metathesis with organic cations (DC⁺) (Fig. 4). We developed a versatile procedure for the cation metathesis, which allows the use of various DC⁺ cations. Fullerene is reduced with sodium ethanethiolate (EtSNa) in the presence of the organic salt $DC^+ \cdot Hal^-$ (Hal = I, Br, or Cl). The degree of reduction of fullerene with thiolates depends on the solvent polarity.83,84 The use of a $C_6H_4Cl_2-o$ —PhCN solvent mixture (15 : 1) results in selective reduction of fullerene to the radical-anion state (1-).^{52,53,76} Sodium halides, salts with organic cations, and sodium ethanethiolate are poorly soluble in this solvent mixture and can be filtered off after reduction (0.5-1 h). Reduced fullerene remains in solution as the $(DC^+) \cdot (C_{60}^{-})$ salt. The advantage of this method is the absence of overreduction of fullerene even in the presence of a large (50-fold) molar excess of the reagent.

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Fig. 4. Methods for the synthesis of neutral and ionic fullerene complexes.

The molecular complexes of fullerenes can be synthesized with different rather weak donors (DC[']), such as metalloporphyrins,^{59–70} metal dithiocarbamates,⁸⁵ amines,⁸⁶ aromatic hydrocarbons,^{87,88} tetrathiafulvalenes,^{2,3,78} etc.^{2–4} (see Fig. 4). These complexes exhibit a large structural diversity. However, the neutral ground state of the complexes results in the absence of conductivity and magnetic ordering.

With the aim, on the one hand, of exploiting high potential of donors DC' to form different structures of fullerene compounds and, on the other hand, with the aim of synthesizing complexes with fullerenes in the charged radical-anion state, we developed a multicomponent approach, in which two donors (DC and DC') are used. A strong donor DC can reduce fullerene or is a small cation (DC⁺). Another larger donor (DC^{\prime}) remains neutral and defines the structure of the resulting complex (see Fig. 4). The { $(Cr^{I}(C_{6}H_{6})_{2}^{\cdot +}) \cdot (Co^{II}TPP \cdot Ful^{-}) \cdot$ ·C₆H₄Cl₂} compound (Ful is fullerene) containing $Cr(C_6H_6)_2$ as the strong donor (DC), which reduces fullerene, and Co^{II}TPP as the neutral donor DC' is an example of such complexes. Different donors and cations, such as TDAE, Cr(C₆H₆)₂, MDABCO⁺, DMP⁺, MP⁺, and DMETEP⁺, can be used as DC; CTV, $Pd(dbdtc)_2$, Co^{II}TPP, Co^{II}OEP, and Co^{II}TMPP can serve as DC² (see Fig. 3).

In solution, fullerene radical anions are very sensitive to oxygen. Because of this, crystals of ionic compounds were synthesized under anaerobic condition in a box filled with an inert gas, the oxygen and water content being lower than 1 promille. The solvents were thoroughly purified from oxygen and water (three freezing—evacuation—filling with argon—thawing cycles). In the crystalline state, the ionic complexes (DC⁺) \cdot (C₆₀^{·-}) are more stable to oxidation (except for complexes with metalcontaining cations). Multicomponent ionic complexes containing the neutral donor component DC' have the highest stability (remain unchanged for several days or more).

The general method for the synthesis of ionic complexes is based on diffusion of hexane into a solution



Fig. 5. Diffusion cell for the crystal growth of ionic complexes.

containing the ionic compound $(DC^+) \cdot (Ful^-)$. The multicomponent complexes $(DC^+) \cdot (Ful^-) \cdot DC'$ were synthesized by the addition of an excess of the second donor component (DC') to the reaction solution (Fig. 5). In these reactions, $C_6H_4Cl_2$ or the $C_6H_4Cl_2$ —PhCN (15:1), C_6H_6 —DMF (14:2), or C_6H_6 —PhCN (12:4) mixture were used as the solvent. Slow diffusion (1–2 months) afforded single crystals suitable for X-ray diffraction. The resulting crystals were initially identified by IR, UV—Vis, and NIR spectroscopy. Then all complexes were characterized by elemental analysis and magnetic measurements (ESR in the range of 4–293 K and SQUID (a superconducting interference detector) in the range of 1.9–300 K). The crystal structures of most of compounds were studied.

The compositions of compounds 1-20 and the temperature ranges of existence of dimers and coordinatively bound anions are given in Table 1. The dimers and the coordinatively bound anions exist at temperatures lower than T_1 . In the range $T_1 < T < T_2$, the C-C and Co-C bonds undergo dissociation. At $T > T_2$, a monomeric phase or uncoordinated cobalt(II) porphyrinate and fullerene radical anions are formed (Scheme 1).

Complex	Type of the resulting structure	Dissociation temperature/K		Refer- ence
		T_1	<i>T</i> ₂	
$(Cp^*_2Cr^+) \cdot (C_{60}^{-}) \cdot (C_6H_4Cl_2)_2$ (1)	σ Dimer (C ₆₀ ⁻) ₂	200	230	45, 46
$\{Cr^{I}(C_{6}H_{6})^{*+}\} \cdot (C_{60}^{*-}) \cdot C_{6}H_{4}Cl_{2}$ (2)	σ Dimer $(C_{60}^{-})_2$	160	240	46, 47
$\{Cr^{I}(C_{6}H_{6})^{2}, *^{+}\} \cdot (C_{60}, *^{-}) \cdot PhCN(3)$	σ Dimer $(C_{60}^{-})_2$	240	>300	46
$\{Cr^{I}(C_{6}H_{6})^{2}, +\}_{2}, (C_{70})_{2}, (C_{6}H_{4}Cl_{2})_{2}, (4)$	Dimer $(C_{70}^{-})_2$	260	>300	46
$(Cp_{2}Co^{+}) \cdot (C_{60} \cdot -) \cdot C_{6}H_{4}Cl_{2}$ (5)	σ Dimer $(C_{60}^{-})_2$	250	350	46
$(Cp_{2}Co^{+})_{2} \cdot (C_{70}^{-})_{2} \cdot C_{6}H_{4}Cl_{2}$ (6)	Dimer $(C_{70}^{-})_2$	>300	_	46
$(Cs^{+})_{2} \cdot (C_{70}^{-})_{2} \cdot CTV \cdot (DMF)_{7} \cdot (C_{6}H_{6})_{0.75} (7)$	Dimer $(C_{70}^{-})_{2}^{-}$	360	390	46, 54
$(Cs^{+})_{2} \cdot (C_{60}^{-})_{2} \cdot CTV \cdot (DMF)_{6}$ (8)	σ Dimer $(C_{60}^{-})_2$	140	220	49
$(Cs^{+})_{2} \cdot (C_{70}^{-})_{2} \cdot (DMF)_{10}$ (9)	Dimer $(C_{70}^{-})_2$	>300	_	46
$\{Cr^{I}(C_{6}H_{6})^{2}, +\} \cdot (C_{60}, -) \cdot \{Pd(dbdtc)_{2}\}_{0,5}$ (10)	σ Dimer $(C_{60}^{-})_2$	150	170	50
$\{(MDABCO^{+}) \cdot Co^{II}TMPP\}_{2} \cdot (C_{60}^{-})_{2} \cdot (C_{6}H_{4}Cl_{2})_{2} \cdot (PhCN)_{15} (11)$	π Dimer (C ₆₀ ⁻) ₂	>300	_	52
$(DMETEP^+)_2 \cdot (C_{60}^-)_2 \cdot \{(Mn^{II}TPP)_2 \cdot DMP\} \cdot (C_6H_4Cl_2)_5 (12)$	σ Dimer (C ₆₀ ⁻) ₂ (86%),	320	360	53
	π Dimer (C ₆₀ ⁻) ₂ (14%)			
$(Cr^{I}(C_{6}H_{6})_{2}^{*+})_{1,7} \cdot \{(Co^{II}TPP \cdot C_{60})_{2}^{1.7-}\} \cdot (C_{6}H_{4}Cl_{2})_{3,3}$ (13)	$\sigma - \{Co^{II}TPP \cdot (C_{60}^{-})\}$	>300	_	74
$(MP^+) \cdot \{Co^{II}TPP \cdot (C_{60}^{-})\} \cdot (C_6H_4Cl_2)_{1,2} $ (14)	σ -{Co ^{II} TPP·(C ₆₀ ⁻)}	>300	_	77
$(Cr^{I}(C_{6}H_{6})_{2}^{+})_{2} \cdot \{Co^{II}TPP \cdot (C_{60}(CN)_{2}^{-})\} \cdot (C_{60}(CN)_{2}^{+}) \cdot (C_{60}(CN)_{2}^$	$\sigma - \{ Co^{II} TPP \cdot (C_{60}(CN)_2^{-}) \}$	>300	_	73, 74
$(TDAE^{+}) \cdot \{Co^{II}TPP \cdot (C_{60}^{-})\}$ (16)	σ -{Co ^{II} TPP·(C ₆₀ ⁻)}	190	>300	75
$(TMP^+) \cdot \{Co^{II}OEP \cdot (C_{60}^-)\} \cdot (PhCN)_{0.75} \cdot (C_6H_4Cl_2)_{0.25}$ (17)	σ -{Co ^{II} OEP·(C ₆₀ ⁻)}	>300	_	76
$\{(MDABCO^{+}) \cdot Co^{II}OEP \cdot (C_{60}^{-})\} \cdot (PhCN)_{0.67} \cdot (C_{6}H_{4}Cl_{2})_{0.33}$ (18)	$(MDABCO^+) \cdot Co^{II}OEP \cdot (C_{60}^-)$	50	250	76
$(Cs^+) \cdot Co^{II}TPP \cdot (C_{60}^{-}) \cdot (PhCN)_{1.64} (C_6H_4Cl_2)_{0.36} \cdot MeCN$ (19)	Uncoordinated Co ^{II} TPP and C_{60} · –	Is not	formed	77
$(DMP^{+})_{2} \cdot (C_{70}^{-})_{2} \cdot (Co^{II}TPP)_{2} \cdot (C_{6}H_{4}Cl_{2})_{2}$ (20)	Dimer $(C_{70}^{-})_2$	>300	—	**

Table 1. Compositions of the complexes and the dissociation temperatures of dimers and coordinatively bound anions*

* TMPP is tetrakis(4-methoxyphenyl)porphyrinate, DMP^+ is the N,N'-dimethylpyrazolium cation, and TMP^+ is the tetramethylphosphonium cation.

** D. V. Konarev, S. S. Khasanov, G. Saito, and R. N. Lyubovskaya, unpublished data.

Scheme 1

Dimerization:

$$DC^{+})_{2} \cdot [(Ful^{-})_{2}] (T < T_{1}) \rightleftharpoons$$
Dimeric phase
$$\implies 2 [(DC^{+}) \cdot (Ful^{-})] (T > T_{2})$$
Monomeric phase
(1-11)

Coordination:

 $(DC^+) \cdot \{(Co^{II}Porph) \cdot (Ful^-)\} (T < T_1) \implies$ Coordinatively bound anions

 $\begin{array}{c} \longleftarrow (DC^+) \cdot (Co^{II}Porph) \cdot (Ful^{--}) \ (T > T_2) \\ Uncoordinated components \end{array} \tag{12-20}$

Porph is porphyrin

2. Formation of dimers of negatively charged fullerenes

2.1. Dimerization of C_{60} [•] in $(Cp*_2Cr^+) \cdot (C_{60}^{\bullet}) \cdot (C_6H_4Cl_2)_2$ (1).^{45,46} 2.1.1. Structural aspects of dimerization in compound 1. The UV—Vis spectra show that complex 1 exists in the ionic state with a total charge transfer

from the Cp*₂Cr donor to the C₆₀ molecule^{45,46} because the first oxidation potential of Cp*₂Cr $(E^{+/0} = -1.04 \text{ V})^{80}$ is substantially more negative than the first reduction potential of C₆₀ $(E^{0/-} = -0.44 \text{ V})$.⁷⁹ The IR spectra also indicate that the C₆₀ ⁻ radical anions exist at room temperature in the monomeric state (upon dimerization, new absorption bands appear in the IR spectrum⁸⁹).

A fragment of the crystal structure of **1** at 300 K is shown in Fig. 6, *a*. The monomeric C_{60} ^{•–} radical anions are orientationally disordered (undergo virtually free rotation), the $C_6H_4Cl_2$ molecules are disordered over two orientations, whereas the $Cp^*_2Cr^+$ cations are ordered (are omitted in Fig. 6, *a*). The C_{60} ^{•–} radical anions form zigzag chains along the diagonal of the *ac* plane. The distance between the centers of C_{60} ^{•–} in the chains is 10.10 Å (in pure C_{60} fullerene, this distance is 10.02 Å at 293 K).⁹⁰

Cooling of compound 1 to temperatures lower than 220–200 K leads to reversible structural changes. The monoclinic cell is retained, but the *c* crystal axis is doubled (Table 2). A comparison of one-half of the unit cell volume at T < 200 K with the unit cell volume before the transition shows that the volume decreases by more than 300 Å³ upon dimerization. At 200 K, singly bonded dimers



Fig. 6. Crystal structures of the monomeric and dimeric phases of complex 1 at 300 (*a*) and 100 K (*b*)⁴⁶. Zigzag chains of C_{60}^{-} are indicated by dashed lines.

 $(C_{60}^{-})_2$ (σ dimers) are formed. However, these dimers are statistically disordered over two orientations (these orientations are related by a rotation axis about the longer axis of the dimer). A decrease in the temperature leads to an increase in the occupancy of one orientation and a decrease in the occupancy of another. At 100 K, the ratio between two orientations is 75 : 25 (all geometric parameters of the $(C_{60}^{-})_2$ dimer were determined for the orientation with a higher occupancy). The σ dimer has the C_{2h} symmetry. In this case, the C_{60}^{-} anions are in *trans* positions relative to one another (see Fig. 2, *a*), which has been predicted theoretically.^{91,92} The average 6–6 and 6–5 bond lengths in fullerene (except for the sp³-hybridized C atoms) are 1.391(21) and 1.445(21) Å, respectively. The C–C bond length between the C_{60}^{-} anions is

Table 2. Changes in the unit cell parameters of 1 upon dimerization⁴⁶

Parameter	300 K	100 K
Molecular formula	C ₁₈₄ H ₇₆ Cl ₈ Cr ₂	C ₃₆₈ H ₁₅₂ Cl ₁₆ Cr ₄
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	$P2_1$
a/Å	23.167(5)	22.973(1)
b/Å	20.983(5)	20.785(1)
c/Å	14.609(2)	24.747(1)
β/deg	123.415(8)	106.387(3)
$V/Å^3$	5928(2)	11247.7(9)
Ζ	2	2
$ ho_{calc}/g\ cm^{-3}$	1.498	1.579

1.597(7) Å, which is substantially larger than the normal C–C bond length (1.541(3) Å)⁹³ and is rather close to the theoretically predicted value (1.618 Å).⁹² In the dimeric phase, the zigzag chains of C_{60}^- are retained. However, the distances between the centers of C_{60}^- are changed (see Fig. 6, *b*). In the dimer, these distances decrease to 9.28 Å. The distance between the centers of C_{60}^- of the adjacent dimers is 9.91 Å.

Since the $(C_{60}^{-})_2$ dimer in complex **1** is singly bonded, it is less stable than the neutral $(C_{60})_2$ dimer containing two shorter C–C bonds $(1.575(7) \text{ Å}).^{24}$ Actually, the dissociation temperature of $(C_{60}^{-})_2$ (200–230 K) is substantially lower than that of the neutral $(C_{60})_2$ dimer $(423-448 \text{ K}).^{24}$ The dissociation energy for $(C_{60}^{-})_2$ in complex **1** is as low as 63 ± 4 kJ mol⁻¹.⁴⁶

2.1.2. Changes in the magnetic properties of complex 1 upon dimerization. At 300 K, the magnetic moment (μ_{eff}) of complex 1 is 4.20 $\mu_{\rm B}$ (Fig. 7, *a*), which corresponds to the contribution of $\operatorname{Cp}_2\operatorname{Cr}^+(S=3/2)$ and $\operatorname{C}_{60}^{\bullet-}(S=1/2)$ (calculated $\mu_{eff} = 4.27 \ \mu_B$). A similar magnetic moment (4.20 μ_B) was found for the ionic complex (Cr^{III}TPP⁺). • $(C_{60}^{\bullet^{-}}) \cdot (THF)_3$, in which $Cr^{III}TPP^+$ also has the spin state S = 3/2, and C_{60} - has the spin $S = 1/2.^{29}$ A decrease in the temperature in a range of 230-200 K leads to a reversible decrease in the magnetic moment of complex 1 to 3.85 μ_B (see Fig. 7, *a*). This is associated with the formation of diamagnetic $(C_{60})_2$ dimers and the disappearance of the contribution of the spins of C_{60} . Therefore, at temperatures lower than 200 K, only the spins of $Cp_{2}^{*}Cr^{+}$ contribute to the magnetic moment $(\mu_{eff} = 3.87 \ \mu_{B})$. Dimerization is reversible with small hysteresis (2 K). The dimeric phase is characterized by the Weiss constant of -1 K, which is indicative of weak antiferromagnetic interactions between spins, resulting apparently in a decrease in the magnetic moment of complex 1 at temperatures lower than 30 K (see Fig. 7). However, antiferromagnetic ordering of spins was not observed down to 1.9 K.

The ESR spectrum of complex 1 at room temperature shows no signals. In the ESR spectrum of the



Fig. 7. Temperature dependences of the magnetic moments of complexes 1 (a) and 2 (b) in the range of $1.9-300 \text{ K.}^{46}$

 $(Cr^{III}TPP^+) \cdot (C_{60} \cdot -) \cdot (THF)_3$ complex described earlier, signals are also absent in the temperature range of 4-300 K.²⁹ Presumably, the monomeric $C_{60} \cdot -$ radical anion and the $Cp_2^*Cr^+$ cation give one very broad signal with the averaged g factor rather than two signals as a consequence of an exchange interaction. To validate this assumption, we measured the ESR spectra of complex 1 with increasing the temperature up to 410 K. Actually, a very broad ESR signal with g = 2.2210 and a half-width (ΔH) larger than 1000 G appears at temperatures higher than 320 K. An increase in the temperature leads to a substantial narrowing of this signal to $\Delta H = 730$ G and a shift of the g factor to 2.1483 at 410 K.⁴⁹

A new ESR signal appears upon cooling of complex 1 below 230 K. The intensity of this signal rapidly increases with decreasing temperature to 200 K. Upon a further decrease in the temperature, the intensity of the ESR signal increases inversely proportional to the temperature. At 4 K, the signal is asymmetric, characterized by the parameters $g_{\perp} = 3.974$ ($\Delta H = 70$ G) and $g_{\parallel} = 2.013$ ($\Delta H = 55$ G), and belongs to the isolated Cp*₂Cr⁺ cation (the (Cp*₂Cr⁺) \cdot (PF₆⁻) salt gives a similar asymmetric ESR signal with $g_{\perp} = 4.02(1)$ and $g_{\parallel} = 2.001(1)^{80}$). The temperature, at which a new signal appears in the ESR spectrum of complex 1, is close to the dimerization temperature. Therefore, the formation of diamagnetic $(C_{60}^{-})_2$ dimers disrupts an interaction between the paramagnetic $Cp*_2Cr^+$ and $C_{60}^{\cdot-}$ ions characteristic of the monomeric phase and results in the contribution of the isolated $Cp*_2Cr^+$ cations to the dimeric phase.

The C_{70} · – radical anions in the ionic compound $(Cp*_2Cr^+) \cdot (C_{70}^-) \cdot C_6H_5Me$ exist as diamagnetic $(C_{70}^-)_2$ dimers, which are stable up to 300 K (ESR data).⁵⁵

2.2. Dimerization of fullerene radical anions in complexes with bis(benzene)chromium.^{46,47} Bis(benzene)chromium and its substituted analogs are widely used for the synthesis of ionic complexes with fullerenes.^{40,43,44,51,58,94} We synthesized the { $Cr^{I}(C_{6}H_{6})_{2}^{+}$ } · (C_{60}^{-}) · $C_{6}H_{4}Cl_{2}$ (2), { $Cr^{I}(C_{6}H_{6})_{2}^{+}$ } · (C_{60}^{-}) · PhCN (3), and { $Cr^{I}(C_{6}H_{6})_{2}^{++}$ } · ($C_{70}^{-})_{2}$ · $C_{6}H_{4}Cl_{2}$ (4) compounds, which have the ionic ground state with the monomeric C_{60}^{-} (2 and 3) radical anion and the ($C_{70}^{-})_{2}$ dimer (4) at room temperature.⁴⁶

At 300 K, the magnetic moment of complex 2 is 2.45 $\mu_{\rm B}$, which corresponds to the contribution of $Cr^{I}(C_{6}H_{6})_{2}^{*+}$ (S = 1/2) and C_{60}^{*-} (S = 1/2) (see Fig. 7, b). At 240-300 K, the Weiss constant is negative (-18 K) and is indicative of the antiferromagnetic character of interactions between spins. The magnetic moment reversibly decreases at 240–160 K to 1.73 μ_B (see Fig. 7, b). Therefore, the contribution of C_{60} - disappears at T < 160 K due to dimerization, and only the contribution of the spins of $Cr^{I}(C_{6}H_{6})_{2}$ · + ($\mu_{eff} = 1.73 \mu_{B}$) persists. The temperature dependence of magnetic susceptibility of complex 2 at $T \le 160$ K follows the Curie—Weiss law with the Weiss constant of -0.5 K. At room temperature, the ESR spectrum of complex 2 shows one Lorenz signal with the g factor of 1.9913, whose value is intermediate between the values characteristic of $Cr^{I}(C_{6}H_{6})_{2}$ · + $(g = 1.986)^{95}$ and C_{60} · - (g = 2.000-1.996).³⁹ This is evidence of an exchange interaction between the spins of the $Cr^{I}(C_{6}H_{6})_{2}$ + radical cation and the C_{60} - radical anion. Cooling of complex 2 in the temperature range of 240–160 K leads to a shift of the g factor to g = 1.986characteristic⁹⁵ of the $Cr^{I}(C_{6}H_{6})_{2}$ + radical cation. This behavior is consistent with the formation of diamagnetic $(C_{60})_2$ dimers at 240–160 K. Interesting features of dimerization in complex 2 are a rather large transition range (80 K) and two steps in the temperature dependence of the magnetic moment with the transition point at 200 K, at which an approximately half of dimers is formed (see Fig. 7, b). This behavior may be associated with the fact that the complex contains two types of dimers, that differ in thermal stability (the difference is ~40 K).

The crystal structure of complex **2** was studied at 250 and 90 K. At 250 K, the C_{60} ^{•-} radical anions are monomeric and orientationally disordered. There are zigzag chains consisting of C_{60} ^{•-} radical anions oriented along the *a* axis; the distances between the centers of C_{60} ^{•-} are



Fig. 8. Crystal structure projected along the b axis for the monomeric (a) and dimeric (b) phases of complex 2 at 250 and 90 K, respectively.⁴⁷ The C_{60} · – radical anions in the monomeric phase are disordered and are shown by circles. The distances between the centers of the C_{60}^{-} anions (Å) are given.

10.052 and 10.279 Å (Fig. 8, *a*).47 The former distance is smaller than the van der Waals diameter of C_{60} (10.18 Å). In this case, shortened C...C contacts are formed. On the contrary, the latter distance is too long for the formation of such contacts. It is these chains where dimerization of C_{60} · - radical anions occurs, dimerization being observed not only in pairs with the shortest distance between the centers (10.052 Å) but also in pairs of the second type. Apparently, dimerization of C_{60} • – radical anions in pairs with the 10.052 Å distance at 240-200 K leads to a contraction of the crystal lattice, which makes possible dimerization in $C_{60}{\:\ensuremath{^{-}}}$ pairs with the 10.279 Å distance at 200–160 K. The dimers generated from pairs of C_{60} . radical anions with different distances between the centers (10.052 and 10.279 Å) differ in the geometric parameters. The distances between the centers of C_{60}^{-} in the dimers are 9.262 and 9.271 Å. The C-C bond lengths between the C_{60}^{-} anions are 1.585(5) and 1.595(5) Å, respectively (see Fig. 8, b). Dimerization in complex 2

ization ⁴⁷	-	
Parameter	250 K	90 K
Molecular formula	C ₇₈ H ₁₆ Cl ₂ Cr	C ₇₈ H ₁₆ Cl ₂ Cr
Space group	$P2_1/c$	$P\overline{1}$
a/Å	15.604(4)	15.6010(13)

Table 3. Changes in the unit cell parameters of 2 upon dimer-

Molecular formula	C ₇₈ H ₁₆ Cl ₂ Cr	C ₇₈ H ₁₆ Cl ₂ Cr
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\overline{1}$
a/Å	15.604(4)	15.6010(13)
b/Å	15.313(4)	14.6619(12)
c/Å	19.461(5)	19.7463(16)
α/deg	_	90.973(3)
β/deg	112.225(8)	112.455(2)
γ/deg	_	86.799(3)
V/Å ³	4305(2)	4167.8(6)
Ż	4	4
$ ho_{calc}/g \ cm^{-3}$	1.660	1.715

leads to a lowering of the unit cell symmetry from monoclinic to triclinic (Table 3) and a decrease in the unit cell volume by ~140 Å³.

In complex 3, dissociation of the dimers starts at a temperature higher than 240 K. Hence, the magnetic moment of complex **3** is as small as 2.12 μ_B even at 300 K (the calculated magnetic moment for a system consisting of two uncoupled spins S = 1/2 is 2.45 $\mu_{\rm B}$). This is evidence that at 300 K only a part of dimers undergo dissociation. The magnetic moment of the dimeric phase is 1.73 μ_B , and the Weiss constant is close to zero, which is indicative of the absence of a magnetic interaction between the spins of $Cr^{l}(C_{6}H_{6})_{2}$.^{+,46}

At 260 K, the magnetic moment of complex 4 is 1.64 $\mu_B,$ and it increases to 1.78 μ_B at 300 K. The ESR signal of complex 4 has g = 1.986 in the temperature range of 293–4 K, which is characteristic⁹⁵ of $Cr^{I}(C_{6}H_{6})_{2}$ ⁺. Therefore, the spins are localized primarily on $Cr^{I}(C_{6}H_{6})_{2}$ + ($\mu_{eff} = 1.73 \mu_{B}$). A small contribution of C_{70} · - radical anions is observed only at T > 260 K, at which dissociation of the diamagnetic $(C_{70})_2$ dimers starts.

Based on the data on the known fullerene complexes with substituted bis(arene)chromium derivatives, the influence of the size of the solvent and bis(arene)chromium molecules and the type of fullerene on stability of σ dimers can be analyzed (Table 4). An increase in the number of substituents in the bis(arene)chromium molecule leads to an increase in the size of the cations. The complex with the largest $Cr^{I}(C_{6}H_{3}Me_{3})_{2}$ ⁺ cation has the lowest dissociation temperature, whereas complexes with the $Cr^{I}(C_{6}H_{5}Me)_{2}$ + and $Cr^{I}(C_{6}H_{6})_{2}$ + cations are characterized by similar dissociation temperatures. The evident tendency to stabilization of the dimeric state $C_{60} < C_{70} <$ $< C_{60}(CN)_2$ is observed in a series of fullerene complexes with $Cr(C_6H_6)_2$. The size of the solvent molecule also affects the type of the resulting structure (polymeric or dimeric) and the dissociation temperature of dimers.

Complex	T/K	Reference
$Cr(C_6H_6)_2 \cdot C_{60}$	220-300	58
$Cr(C_6H_5Me)_2 \cdot C_{60}$	250	43
$Cr(C_{6}H_{3}Me_{3})_{2} \cdot C_{60}$	<170	51
	(without a phase transition)	
$Cr(C_6H_6)_2 \cdot C_{60} \cdot CS_2$	—	40
$Cr(C_6H_6)_2 \cdot C_{60} \cdot C_6H_4Cl_2$	160-240	46
$Cr(C_6H_6)_2 \cdot C_{60} \cdot PhCN$	240->300	46
$Cr(C_6H_6)_2 \cdot C_{70} \cdot C_6H_4Cl_2$	260->300	46
$Cr(C_6H_6)_2 \cdot C_{70} \cdot C_6H_5Me$	300->400	55
$Cr(C_6H_6)_2 \cdot C_{60}(CN)_2$	>380	58

 Table 4. Dissociation temperatures of the dimers of fullerene radical anions in ionic complexes

2.3. Dimerization of fullerene radical anions in complexes with cobaltocene.⁴⁶ The $(Cp_2Co^+) \cdot (C_{60} \cdot -) \cdot$ $\cdot C_6 H_4 Cl_2$ complex (5) exists in the diamagnetic state in the temperature range of 1.9-250 K due to the formation of diamagnetic $(C_{60}^{-})_2 \sigma$ dimers and Cp_2Co^+ cations. Only ~3.3% of spins of the total number of C_{60} molecules give a paramagnetic contribution. This is associated with the presence of a small amount of monomeric C_{60} - radical anions, which cannot undergo dimerization due apparently to the presence of defects. At T > 250 K, the magnetic moment of 5 increases up to $1.52 \mu_B$ (350 K) as a result of dissociation of $(C_{60}^{-})_2$. The ionic state of complex 5 with monomeric C_{60} - radical anions is justified by characteristic absorption bands of the $C_{60}{}^{\scriptscriptstyle \bullet}{}^{\scriptscriptstyle -}$ radical anion in the IR and near-IR spectra and the appearance of the intense ESR signal of the C_{60} ⁻ radical anion^{2,39} $(g = 1.9988 \text{ and } \Delta H = 39.7 \text{ G at } 293 \text{ K}).^{46}$ The $(Cp_2Co^+)_2 \cdot (C_{70})_2 \cdot C_6H_4Cl_2$ complex (6) contains $(C_{70}^{-})_2$ dimers, which are stable up to 300 K, and exhibits diamagnetic properties in the temperature range of 1.9-300 K.46

2.4. Dimerization of fullerene radical anions in complexes with cesium.^{46,49,54} The $(Cs^+)_2 \cdot (C_{70}^-)_2 \cdot CTV \cdot (DMF)_7 \cdot (C_6H_6)_{0.75}$ (7) and $(Cs^+)_2 \cdot (C_{60}^-)_2 \cdot CTV \cdot (DMF)_6$ (8) complexes were synthesized using a multicomponent approach. The neutral CTV molecule (see Fig. 3) was introduced into the ionic salts $(Cs^+) \cdot (Ful^-)$ due to the formation of additional coordination bonds between CTV and cesium cations $(O...Cs^+)$ analogously to coordination of alkali metal cations with crown ethers.

The crystal structure of 7 was studied⁵⁴ at 120 K, and the molecular structure of singly bonded $(C_{70}^{-})_2$ dimers was established for the first time. The C_{2h} symmetry of the dimers is substantially lower than that of the starting C_{70} (D_{5h}). The C_{70}^{-} anions in the dimer are in the *trans* conformation with respect to each other (Fig. 9). The average angles for the sp³-hybridized C atoms are 109°, which is close to a tetrahedral geometry. The



Fig. 9. Crystal structure of the dimeric phase of complex 7 at 120 K.⁵⁴ Two crystrallographically independent $(C_{70}^{-})_2$ dimers and two cyclotriveratrylene (CTV) molecules, which are coordinated to four Cs⁺ cations are presented. The disordered *N*,*N*-dimethylformamide and benzene molecules are omitted.

C-C bond length between the C_{70}^{-} anions in the dimer is 1.584(9) Å, whereas the distance between the centers of gravity of two C_{70}^{-} anions is 10.417 Å. The C-C bond length in the $(C_{70}^{-})_2$ dimer is substantially larger than the normal C-C bond length (1.541(3) Å)⁹³ and is intermediate between the C-C bond lengths in the $(C_{60}^{-})_2$ σ dimer (1.597(7) Å)⁴⁵ and the neutral $(C_{60})_2$ dimer (1.575(7) Å).²⁴ The shape of CTV is in good steric agreement with that of the ellipsoidal C_{70}^{-} anion, resulting in the formation of numerous van der Waals contacts between these species.

In the temperature range of 1.9–350 K, complex 7 is diamagnetic and gives a weak asymmetric ESR signal at 293 K, which can be decomposed into three components with $g_1 = 2.0042 \ (\Delta H = 8 \text{ G}), g_2 = 2.0024 \ (\Delta H = 2 \text{ G}), \text{ and}$ $g_3 = 1.9923 (\Delta H = 20 \text{ G}).^{54}$ The number of spins per formula unit of the complex, which was estimated from the integral intensity of the ESR signal, is as small as 0.4%. The signal can be assigned to a small amount of undimerized C₇₀[•] radical anions. Similar ESR signals were recorded for the electrochemically generated C_{70} . radical anion in solution $(g_1 = 2.007, g_2 = 2.003, \text{ and} g_3 = 2.0000)^{79}$ and for the $(Ph_4P^+)_2(C_{70} \cdot)(I^-)$ salt $(g_x = g_y = 1.9996, g_z = 2.0150, \text{ and } g_{av} = 2.0047).^{34}$ Therefore, the $(C_{70})_2 \sigma$ dimers are diamagnetic and give no ESR signals. An increase in the magnetic moment of complex 7 is observed at a temperature higher than 360 K, which may be associated with dissociation of $(C_{70})_2$. At 390 K, the degree of dissociation of the dimers is \sim 90%.

An analogous complex was synthesized⁴⁹ with C_{60} (8). At 293 K, this complex has the ionic ground state and contains monomeric C_{60} ^{•-} radical anions, which give an ESR signal with g = 1.9990 and $\Delta H = 57$ G. The formation of σ dimers is observed at 140–220 K and is accompanied by the transition from the paramagnetic to the diamagnetic state, the intensity of the ESR signal of the C_{60} ^{•-} radical anion being decreased by more than a factor of 30 (like in all other cases, several percentage of C_{60} ⁻ radical anions remain undimerized). Therefore, the dissociation temperature of the $(C_{60}^{-})_2$ dimers in complex **8** is substantially lower than that of the $(C_{70}^{-})_2$ dimers in complex **7**. An analogous situation is observed for all known compounds of C_{60} and C_{70} , *viz.*, Cp^*_2Cr (**1** and $(Cp^*_2Cr^+) \cdot (C_{70}^{-}) \cdot C_6H_5Me^{55}$), $Cr(C_6H_6)_2$ (**2** and **4**), and Cp_2Co (**5** and **6**).

In the absence of CTV in DMF, the salt of C_{70} fullerene with DMF-solvated Cs⁺ cations, $(Cs^+)_2 \cdot (C_{70}^-)_2 \cdot (DMF)_{10}$ (9) can be prepared, and this salt contains $(C_{70}^-)_2$ dimers stable up to 300 K.⁴⁶

2.5. Dimerization of C_{60} - radical anions in the ${Cr^{I}(C_{6}H_{6})_{2}^{+}} \cdot (C_{60}^{-}) \cdot {Pd(dbdtc)_{2}}_{0.5} \text{ complex (10).}^{50}$ Complex 10 was synthesized by reduction of fullerene with bis(benzene)chromium, palladium(II) dibenzyldithiocarbamate acting as a structure-forming neutral molecule.⁵⁰ In the structure of 10 (solved at 90 K), the strongly deformed layers of C_{60} \cdot – radical anions alternate with the layers of Pd(dbdtc)₂, and the $Cr^{I}(C_{6}H_{6})_{2}$ + radical cations are located between the layers (Fig. 10). The C_{60} ·radical anions form pairs inside the layers with a short C...C distance (3.092(2) Å), which is substantially smaller than the sum of the van der Waals radii of two C atoms (3.42 Å).⁹⁶ This is indicative of the monomeric state of C_{60} . The diamagnetic $(C_{60})_2$ dimers are formed in complex 10 upon cooling at 150-130 K and undergo dissociation upon heating at 150-170 K, which is accompanied by the corresponding change in the magnetic moment (Fig. 11). The dimerization-dissociation hysteresis is ~20 K (see Fig. 11, the inset). Nowadays, this is the largest hysteresis for the known complexes. The formation temperatures of $(C_{60}^{-})_2$ dimers varies from 220 to 360 K. Therefore, complex 10 is characterized by the lowest dimerization temperature (150-130 K) of all the known complexes. The ESR spectrum of the monomeric phase contains a Lorenz signal with g = 1.9934 and a half-width of 41 G. This g factor is intermediate between those for $Cr^{I}(C_{6}H_{6})_{2}^{\cdot +}$ (g = 1.986)⁹⁵ and $C_{60}^{\cdot -}$ (g = 2.000 - 1.996),^{2,39} which is indicative of an exchange



Fig. 10. Crystal structure of complex **10** at 90 K.⁵⁰ The short (3.092(2) Å) van der Waals C...C contacts between the C_{60} ⁻⁻ radical anions are indicated by dashed lines.



Fig. 11. Temperature dependence of the magnetic moment of complex 10 in the range of 1.9-300 K. The temperature dependences of the magnetic moment measured in the cooling and heating modes are shown in the inset.⁵⁰

interaction between these radical ions. Upon dimerization in complex **10**, the shape of the ESR signal changes, and its intensity is halved. The signal becomes asymmetric with two components at $g_1 = 1.9969$ ($\Delta H = 22.4$ G) and $g_2 = 1.9826$ ($\Delta H = 23.2$ G). A similar asymmetric ESR signal was observed⁹⁵ for the isolated Cr^I(C₆H₆)₂⁺⁺ radical cation.

We found that the dimerization temperature depends on the cooling rate. The onset of dimerization was detected by ESR spectroscopy. It appeared that at a high cooling rate, the dimerization temperature decreases. For example, cooling of complex **10** for 10 min from 293 to 100 K leads to a shift of the temperature of the onset of dimerization from 140 to 60 K. In the study of the crystal structure of **10**, cooling of the crystal down to 90 K was performed during 10 s, which apparently made it possible to retain the monomeric phase of **10** at 90 K.⁵⁰

2.6. Formation of the doubly bonded $(C_{60}^{-})_2$ dimer.⁵² The { $(MDABCO^+) \cdot Co^{II}TMPP_2 \cdot (C_{60}^{-})_2 \cdot (C_6H_4Cl_2)_{2.5} \cdot (PhCN)_{1.5}$ complex (11) containing this dimer was synthesized by the addition of the neutral $Co^{II}TMPP$ molecule to the $(MDABCO^+) \cdot (C_{60}^{-})$ salt. The N atom of the MDABCO⁺ cation is coordinated to the Co atom of the CO^{II}TMPP molecule giving rise to the coordinatively bound $(MDABCO^+) \cdot Co^{II}TMPP$ cation (Co-N, 2.385(3) Å; Fig. 12). Then this cation forms complex 11 with C_{60}^{-} . There are two MDABCO⁺ cations per dimer in complex 11. Hence, the formal charge of the dimer is (2–). The IR and near-IR spectra prove this assumption.⁵²

The crystal structure of **11** was determined at 120 K.⁵² The C_{60}^{-} anions in the dimer are linked to each other by



Fig. 12. Fragment of the crystal structure of complex **11** at 120 K.⁵² The $(C_{60}^{-})_2 \pi$ dimer and the coordinatively bound (MDABCO⁺) \cdot Co^{II}TMPP cations are presented. The N atoms (N⁺) in the MDABCO⁺ cation bearing a positive charge are labeled.

two C–C bonds (1.581(3) Å). These bonds are longer than those in the neutral $(C_{60})_2$ dimer (1.575(7) Å)²⁴ but shorter than that in the $(C_{60}^{-})_2 \sigma$ dimer (1.597(7) Å).⁴⁵ The distance between the centers of C_{60}^{-} in the doubly bonded dimer (C-C, 9.07 Å) is substantially shorter than that in the σ dimer (9.28 Å).⁴² The average 6–6 and 5–6 bond lengths in the π dimer (1.395(11) and 1.448(10) Å, respectively), except for the bonds involving sp³-hybridized C atoms, are similar to those for the σ dimer. In complex 11, Co^{II}TMPP is not coordinated to the $(C_{60}^{-})_2$ dimer. The Co...C($(C_{60}^{-})_2$) distances (2.75–2.97 Å) are substantially longer than the analogous distances upon the formation of the Co-C coordination bonds in the $\{Co^{II}TPP \cdot (C_{60}^{-})\}$ anions $(2.28-2.32 \text{ Å})^{74}$ and the Co...C van der Waals contacts in neutral complexes of cobalt(II) porphyrinates with fullerenes (2.58-2.69 Å).66,74 Presumably, the formation of the Co $-C((C_{60}^{-})_2)$ coordination bond is hindered by a competition of the MDABCO⁺ cation located on the opposite side of the porphyrin plane for the coordination site at the Co atom (see Fig. 12), resulting in a deviation of the Co atom toward the N atom of the MDABCO⁺ cation by 0.193 Å.

The $(C_{60}^{-})_2$ dimers in complex **11** are isolated from each other, because they are located inside the cell formed by six coordinated (MDABCO⁺) \cdot Co^{II}TMPP cations (in Fig. 12, only four such cations are shown). Presumably, it is these van der Waals interactions between the (MDABCO⁺) \cdot Co^{II}TMPP cations in this cell that are favorable for the formation of a more compact doubly bonded dimer instead of the commonly observed σ dimer.

In spite of the absence of the Co $-C((C_{60}^{-})_2)$ coordination bond in complex **11**, there is an efficient interaction between the π systems of Co^{II}TMPP and $(C_{60}^{-})_2$ sufficient for an exchange magnetic interaction between these species. Both Co^{II}TMPP and the $(C_{60}^{-})_2$ dimer

contribute to the magnetic moment of complex 11. The magnetic moment is 3.47 μ_B at 300 K, which is similar to the calculated magnetic moment for a system containing four uncoupled spins S = 1/2 ($\mu_{eff} = 3.46 \mu_B$). Two C_{60}^{-} anions, each containing approximately one spin, form a single molecule in the dimer. Hence, this dimer should exist in the biradical state. Actually, the ESR data confirm the presence of spins on the dimer, because the ESR spectrum shows a broad signal of Co^{II}TMPP along with a signal of the C_{60}^{-} anion. Due to a strong exchange interaction between Co^{II}TMPP and $(C_{60}^{-})_2$, both signals have a Lorenz shape and do not exhibit individual features, such as asymmetry or a triplet splitting. The intensity of the ESR signal of the $(C_{60}^{-})_2$ dimer decreases with decreasing temperature. The observed temperature dependence can be described in terms of the triplet state model⁹⁷ with an energy gap between the triplet (S = 1)and singlet (S = 0) levels of $70 \pm 2 \text{ cm}^{-1}$, which is ~10 times smaller than the analogous values for the monomeric fullerene dianion C_{60}^{2-} in solution and in the solid state (600 and 730 cm⁻¹, respectively).^{30,98}

2.7. Formation of two types of dimers in the same compound.⁵³ The (DMETEP⁺)₂ \cdot (C₆₀⁻)₂ \cdot {(Mn^{II}TPP)₂ \cdot DMP} \cdot (C₆H₄Cl₂)₅ complex (12) was prepared by crystallization of the (DMETEP⁺) \cdot (C₆₀⁻) salt with the coordinated (Mn^{II}TPP)₂ \cdot DMP dimer. The unusual DMETEP⁺ cation (see Fig. 3) is generated by the nucleophilic addition of the ethanethiolate anion (EtS⁻) to the dimethyldiazabicyclooctane dication (DMDABCO²⁺). These compounds were used as the starting reagents for reduction of fullerene and cation metathesis.⁵³

The crystal structure of **12** was solved⁵³ at 100 K. The main distinguishing structural feature of complex **12** is the presence of channels formed by four $(Mn^{II}TPP)_2 \cdot DMP$ molecules. The channels are occupied by zigzag chains composed of the alternating $(C_{60}^{-})_2$ dimers and the DMETEP⁺ cations (Fig. 13). It was found that the structure of **12** contains two types of $(C_{60}^{-})_2$ dimers, *viz.*, the σ dimer with an occupancy of 86% and the doubly bonded $(C_{60}^{-})_2$ dimer with an occupancy of 14%. The geometric parameters of these dimers are similar to those found earlier for two types of $(C_{60}^{-})_2$ dimers.

The magnetic moment of complex 12 is 8.3 μ_B in the temperature range of 40–320 K (Fig. 14), which corresponds to the contribution of two high-spin Mn^{II} atoms (S = 5/2 + 5/2, $\mu_{eff} = 8.37 \mu_B$). The Weiss constant (-0.5 K) is indicative of a weak antiferromagnetic interaction between spins in complex 12, resulting in a decrease in the magnetic moment at T < 40 K (see Fig. 14). The contribution of C₆₀ [•] – is not observed at 40–320 K because of dimerization. Although the doubly bonded (C₆₀⁻)₂ dimers are paramagnetic, their contribution is insignificant (no higher than 0.06 μ_B) compared to the contribution of high-spin Mn^{II} because of a low occupancy of the position of this dimer. At a temperature

 π -(C₆₀⁻)₂ (14%)



Fig. 13. Fragment of the crystal structure of complex **12** projected along the *a* axis and the zigzag chains of the $(C_{60}^{-})_2$ dimers and the DMETEP⁺ cations.⁵³ The Mn^{II}TPP porphyrinate forms coordination dimers $(Mn^{II}TPP)_2 \cdot DMP$, in which two porphyrin fragments are linked to each other by the bidentate N, N'-dimethylpiperazine (DMP) ligand.

higher than 320 K, the magnetic moment increases up to 8.66 μ_B (360 K), which corresponds to the appearance of two paramagnetic C_{60} ⁻ radical anions upon dissociation of the diamagnetic $(C_{60}^{-})_2 \sigma$ dimer ($\mu_{eff} =$ 8.72 μ_B). Dissociation of the dimers is accompanied by substantial changes in the ESR spectrum of complex **12**. The dimeric phase is characterized by a complex ESR spectrum with a large number of components in the range from 0 to 7000 G. This spectrum is attributed to an exchange interaction between two Mn^{II} atoms in the (Mn^{II}TPP)₂•DMP coordination dimer. Upon dissociation of σ -(C_{60}^{-})₂ at a temperature higher than 320 K, a new Lorenz signal with g = 2.0179 ($\Delta H = 655$ G) ap-



Fig. 14. Temperature dependence of the magnetic moment of complex 12 in the range of 1.9-360 K.⁵³

pears in the ESR spectrum. The intensity of the latter increases as the temperature increases up to 360 K, whereas the signal characteristic of the dimeric phase virtually disappears. The new signal can be assigned to the paramagnetic $(Mn^{II}TPP)_2 \cdot DMP$ and $C_{60} \cdot -$ species involved in an exchange interaction.

Numerous examples provide evidence that the dissociation temperatures of σ dimers in C₆₀ complexes are substantially different. For example, of all the known σ dimers, the highest temperature (320 K), at which dissociation begins, is observed for complex 12. Apparently, stability of the $(C_{60}^{-})_2 \sigma$ dimers and, consequently, the dissociation temperature substantially depend on the nature of the solvent molecules, cations, and neutral components surrounding the dimer in the crystal structure. Dissociation of dimers leads to a substantial increase in the volume occupied by two individual C_{60} - radical anions. Hence, the environment of the dimer exerts a "pressure" on the latter and can stabilize the dimer, thus increasing the dissociation temperature. Apparently, an increase in the "pressure" leads not only to stabilization of σ dimers but also to an increase in the percentage of doubly bonded $(C_{60}^{-})_2$ dimers, which are more compact than σ dimers (the distances between the centers of C₆₀⁻ are 9.07 and 9.28 Å, respectively). Apparently, this is responsible for the appearance of a small amount of the doubly bonded $(C_{60}^{-})_2$ dimers in complex 12. In the limiting case, like in complex 11, a compound only with the latter dimers is formed.

3. Formation of coordinated {(Co^{II}Porph) · (Ful⁻)} anions

3.1. Coordination of fullerene radical anions to $Co^{II}TPP.^{49,73,74,77}$ The { $Cr^{I}(C_{6}H_{6})_{2}^{++}$ }_{1.7} ·{($Co^{II}TPP. C_{60})_{2}^{1.7-}$ } ·($C_{6}H_{4}Cl_{2}$)_{3.3} (13), (MP⁺) ·{ $Co^{II}TPP. (C_{60}-)$ } ·($C_{6}H_{4}Cl_{2}$)_{1.2} (14), and { $Cr^{I}(C_{6}H_{6})_{2}^{++}$ }₂ · { $Co^{II}TPP \cdot (C_{60}(CN)_{2}^{--})$ } ·($C_{6}H_{4}Cl_{2}$)₃ (15) complexes were synthesized by the introduction of the neutral Co^{II}TPP molecule into the ionic complex (DC⁺) · (Ful⁻), resulting in the formation of Co–C coordination bonds between Co^{II}TPP and the fullerene radical anions. Tetraphenylporphyrinates of other metals (Fe, Cu, and Zn) cannot form stable metal–carbon coordination bonds. Analogous complexes with Fe, Cu, and Zn tetraphenylporphyrinates were not synthesized.

Complex 13 contains two crystallographically independent coordinatively bound (Co^{II}TPP \cdot C₆₀⁻) anions with the Co...C distances of 2.294(10) and 2.319(9) Å (see Fig. 2, *d*). The Co...C distances for three other C atoms nearest to the coordinated C atom are substantially longer (3.004–3.204 Å). This coordination mode corresponds to σ -bonding between Co^{II}TPP and C₆₀⁻. It should be noted that the Co–C bond (2.29–2.32 Å) is

substantially longer that the Co–C bonds in alkylcobalamines (1.99–2.03 Å),⁷² *i.e.*, the Co–C(C₆₀⁻) bond in complex **13** is rather weak. However, it is substantially shorter than the M...C_{Ful} contacts in complexes of neutral fullerenes with metal tetraphenyl- and octaethylporphyrinates (2.55–3.00 Å).^{60,63–71} Therefore, the fullerene radical anions are stronger ligands than neutral fullerenes.

The magnetic moment of complex **13** at 300 K is 2.4 μ_B , which is close to the value of 2.26 μ_B calculated for a system, in which only $\operatorname{Cr}^{I}(\operatorname{C}_{6}\operatorname{H}_{6})_{2}^{*+}$ (S = 1/2) gives a contribution to the magnetic moment. At the same time, this magnetic moment is substantially smaller than $\mu_{eff} = 4.14 \,\mu_B$ calculated for a system, in which all paramagnetic species ($\operatorname{Cr}^{I}(\operatorname{C}_{6}\operatorname{H}_{6})_{2}^{*+}$, $\operatorname{Co}^{II}\operatorname{TPP}$, and $\operatorname{C}_{60}^{*-}$) make a contribution to the magnetic moment. The ESR signal of complex **13** in the temperature range of 4–293 K has g = 1.986, which is characteristic of $\operatorname{Cr}^{I}(\operatorname{C}_{6}\operatorname{H}_{6})_{2}^{*+}$.⁹⁵ Consequently, both coordinatively bound ($\operatorname{Co}^{II}\operatorname{TPP}\cdot\operatorname{C}_{60}^{-}$) anions in complex **13** are diamagnetic and are not observed in the ESR spectrum.⁷⁴

Complex 14 contains the diamagnetic *N*-methylpyridinium cations (MP⁺, see Fig. 3) and the diamagnetic coordinatively bound (Co^{II}TPP \cdot C₆₀⁻) anions stable up to 300 K, due to which this complex is diamagnetic and gives no ESR signals in the temperature range of 1.9–300 K.^{49,77}

Multicomponent complex **15** with dicyanofullerene $C_{60}(CN)_2$ contains the new coordinated $Co^{II}TPP \cdot \{C_{60}(CN)_2^-\}_2$ species (Fig. 15). One $C_{60}(CN)_2^-$ anion forms a coordination bond with $Co^{II}TPP$; the Co...C distance is 2.283(3) Å. The second $C_{60}(CN)_2^{--}$ radical anion



Fig. 15. Fragment of the crystal structure of complex $15.^{73}$ The Co–C coordination bond is indicated by a solid line, and the shortened van der Waals Co^{II}...C(C₆₀(CN)₂^{•–}) contacts are shown by dashed lines.

forms only shortened η^2 -type van der Walls contacts with Co^{II}TPP; the Co...C distances are 2.790(3) and 2.927(3) Å (see Fig. 15).

The magnetic moment of complex **15** is 2.91 μ_B at 300 K, which corresponds to the contribution of three spins S = 1/2 ($\mu_{eff} = 3 \mu_B$), whereas five spins S = 1/2should be present taking into account the composition of this complex. At 293 K, the ESR signal of complex **15** has a single line. At T < 180 K, this line is split into two components ($g_1 = 1.9821$ with $\Delta H = 15$ G and $g_2 = 1.9934$ with $\Delta H = 21$ G at 4 K). The former signal can be assigned to the Cr^I(C₆H₆)₂^{•+} radical cations; the latter signal, to two radical ions (uncoordinated C₆₀(CN)₂^{•-} and Cr^I(C₆H₆)₂^{•+}) having an exchange interaction. From these data it follows that the coordinatively bound (Co^{II}TPP•C₆₀(CN)₂⁻) anions are also diamagnetic.

3.2. Reversible dissociation of $\{Co^{II}TPP \cdot (C_{60}^{-})\}$.⁷⁵ The (TDAE \cdot^+) \cdot {Co^{II}TPP \cdot (C₆₀⁻)} complex (**16**) involves the paramagnetic TDAE⁺⁺ serving as the cation (see Fig. 3). Complex 16 formally contains three paramagnetic species, viz., Co^{II}TPP, TDAE⁺⁺, and C₆₀⁺⁻, with the spin S = 1/2. Hence, the magnetic moment in this system should be 3 μ_B . The real magnetic moment of complex 16 at low temperatures (10–190 K) is 1.45 $\mu_{\rm B}$ (Fig. 16). A decrease in the magnetic moment of complex 16 is associated with the formation of the diamagnetic coordinatively bound ($Co^{II}TPP \cdot C_{60}^{-}$) anions. The ESR spectrum of complex 16 at 4–190 K contains one Lorenz line (g = 2.0030-2.0050 and ΔH = 32 G), which can be assigned to TDAE⁺⁺ (g = 2.0035).⁸² In the temperature range of 190–300 K, the magnetic moment of complex 16 increases ($\mu_{eff} = 1.85 \ \mu_B$ at 300 K, see Fig. 16), the ESR signal is broadened to 242 G (293 K), and the g factor is shifted to higher values (g = 2.0194 at 293 K). Since Co^{II}TPP in fullerene complexes is characterized by $g \cong 2.4$ and $\Delta H = 500 - 600 \text{ G}$ at 293 K,^{61,63} the observed changes



Fig. 16. Temperature dependence of the magnetic moment of polycrystalline complex **16** in the range of 1.9–300 K.⁷⁵ The vertical line corresponds to the beginning of dissociation of $\{Co^{II}TPP \cdot (C_{60}^{-})\}$.

can be attributed to dissociation of the (Co^{II}TPP·C₆₀⁻) anions and the appearance of the contribution of the uncoordinated paramagnetic ESR-active Co^{II}TPP and C_{60} ⁻⁻ species, which can give one broad ESR signal. In the temperature range of 190–300 K, ~20% of the coordinatively bound anions undergo dissociation.

3.3. Characteristic features of coordination of Co^{II}OEP and $C_{60}^{-.76}$ Cobalt(II) octaethylporphyrinate forms the multicomponent complexes (TMP⁺) • {Co^{II}OEP • $\cdot (C_{60}^{-}) \cdot (PhCN)_{0.75} \cdot (C_6H_4Cl_2)_{0.25}$ (17) $(MDABCO^+) \cdot \{(MDABCO^+) \cdot Co^{II}OEP \cdot (C_{60}^-)\} \cdot$ • (PhCN)_{0.67} • ($C_6H_4Cl_2$)_{0.33} (18) with fullerene anions and small cations, such as TMP⁺ and MDABCO⁺. In complex 17, the tetramethylphosphonium (TMP^+) cation is not coordinated to metalloporphyrin (Fig. 17, a), whereas the *N*-methyldiazabicyclooctane cation (MDABCO⁺) complex 18 is coordinated forming the in Co...N(MDABCO⁺) bond with a length of 2.340(1) Å (see Fig. 17, b). Complexes 17 and 18 have similar structures and contain zigzag chains composed of the C_{60}^{-1} anions and cations, which are located in channels formed by Co^{II}OEP molecules. Nevertheless, the difference in the coordination ability of TMP⁺ and MDABCO⁺ results in the formation of different coordination structures in complexes 17 and 18.⁷⁶

In the presence of TMP⁺, complex **17** contains the coordinatively bound {Co^{II}OEP \cdot (C₆₀⁻)} anions analogous to (Co^{II}TPP \cdot C₆₀⁻) (the Co...C(C₆₀⁻) distance is 2.268(1) Å at 100 K; see Figs 17, *a* and 2, *e*). In the temperature range of 4–293 K, complex **17** gives no ESR signals, which is indicative of the diamagnetic state of the {Co^{II}OEP \cdot (C₆₀⁻)} anions and their stability up to room temperature.

Apparently, an additional coordination of MDABCO⁺ to Co^{II}OEP in complex 18 destabilizes the Co...C(C_{60}^{-}) bond. As a result, the Co...C(C_{60}^{-}) bond in 18 is substantially longer than that in 17 (2.508(4) Å at 100 K). In the temperature range of 4-50 K, complex 18 gives no ESR signals (Fig. 18), which is consistent with the formation of the coordinatively bound diamagnetic {(MDABCO⁺)· • $Co^{II}OEP \cdot (C_{60})$ species with the Co–N and Co–C coordination bonds. At a temperature higher than 50 K, a new broad ESR signal appears and its intensity begins to increase (g = 2.1188 and $\Delta H = 520$ G at 293 K). The appearance of this signal is associated with dissociation of Co-C coordination bonds and the formation of the uncoordinated paramagnetic (MDABCO⁺) · Co^{II}OEP and C_{60} · – species. The latter give one ESR signal due to an exchange interaction. These signals are observed in most of ionic fullerene complexes containing two paramagnetic species (C_{60} · – and cations or neutral donors). The integral intensity of the ESR signal in the spectrum of 18 at T > 250 K corresponds to dissociation of all diamagnetic species into paramagnetic species (see Fig. 18). This is the first example of reversible dissociation of the Co-C(C₆₀⁻) coordination σ bond accompanied by the transition from the diamagnetic to the paramagnetic state.

The crystal structure of **18** was determined at 100 K, at which the Co–C coordination bond is virtually formed, because the contribution of the diamagnetic coordinated state to {(MDABCO⁺) · Co^{II}OEP · (C₆₀⁻)} at 100 K is ~90%, as estimated by ESR spectroscopy (see Fig. 18). Therefore, the Co...C distance of 2.51 Å is intermediate between those in the coordinatively bound state, in which both electrons of Co^{II}OEP and C₆₀⁻⁻ are paired to form a Co–C coordination bond, and the uncoordinated state



Fig. 17. Molecular structure of the stable coordinated { $Co^{II}OEP \cdot (C_{60}^{-})$ } anion in complex 17 (*a*) and the coordinated { $(MDABCO^{+}) \cdot Co^{II}OEP \cdot (C_{60}^{-})$ } species in complex 18 (*b*).⁷⁶



Fig. 18. Temperature dependence of the integral intensity of the ESR signal of complex **18**:⁷⁶ the diamagnetic {(MDABCO⁺) · \cdot Co^{II}OEP · (C₆₀⁻)} complex (*a*); the Co–C(C₆₀⁻) coordination bond formation (*b*); the region, in which coordination is absent (*c*). The expected integral intensity of the ESR signal for two uncoupled spins S = 1/2 is indicated by a dashed line. The temperature, at which the crystal structures of complex **18** was established, is shown by an arrow.

containing paramagnetic Co^{II}OEP and C₆₀^{•–}. It is seen that this distance (2.51 Å) is substantially longer than the Co–C bonds in alkylcobalamines $(1.99-2.03 \text{ Å})^{72}$ and complex 17 (2.27 Å).

3.4. Complexes without Co–C coordination bonds^{*}.⁷⁷ In the $(Cs^+) \cdot Co^{II}TPP \cdot (C_{60} \cdot -) \cdot (PhCN)_{1.64}(C_6H_4Cl_2)_{0.36} \cdot MeCN$ complex (19), Co^{II}TPP and the monomeric C₆₀ $\cdot -$ radical anions coexist separately and are not coordinated to each other.

This complex contains the Cs⁺ cation solvated by two benzonitrile molecules and one acetonitrile molecule (Fig. 19). Since the Cs^+ : C_{60} ratio is 1 : 1, the charge on fullerene is 1-. The structure of complex 19 was established at 110 K. It contains zigzag chains formed by the alternating Co^IITPP and C_{60} $\dot{}^-$ species (a fragment of this chain is shown in Fig. 19). Each C_{60} ⁻ radical anion is involved in contacts with two Co^{II}TPP molecules; the Co...C(C₆₀) distances are in the range of 2.55-3.07 Å. These distances are substantially longer than the Co-C distances in the coordinatively bound (Co^{II}TPP•Ful⁻) anions $(2.27-2.32 \text{ Å})^{73,74,76}$ and are similar to the Co...C distances in neutral C₆₀ complexes (2.58–2.70 Å).^{64,66,74} Because of a weak coordination in complex 19, the Co atom does not deviate from the porphyrin plane toward fullerene as opposed to the coordinatively bound



Fig. 19. Fragment of the crystal structure of complex $19.^{77}$ The disordered $C_6H_4Cl_2$ molecules are omitted. The shortened van der Waals contacts with metals (Co, Cs⁺) are indicated by dashed lines.

(Co^{II}TPP·Ful⁻) anions, in which the Co atom deviates toward fullerene by 0.091–0.113 Å.^{73,74,76} Apparently, the Co–C coordination bond in complex **19** is absent because of a large size of the solvated (Cs⁺) • (PhCN)_{1.64} • • MeCN cation, which does not allow the Co^{II}TPP fragment to approach closely the C₆₀ ⁻ radical anion.

The ESR spectrum of complex **19** shows two Lorenz signals with $g_1 = 2.0009$ ($\Delta H = 47.8$ G) and $g_2 = 2.4982$ ($\Delta H = 512$ G). The former signal, which narrows as the temperature decreases (3 G at 4 K), belongs to C₆₀^{•-}, whereas the latter signal is assigned to Co^{II}TPP. These data are in good agreement with the presence of the uncoordinated paramagnetic Co^{II}TPP and C₆₀^{•-} fragments in the complex.

In some ionic compounds, short contacts both between cobalt(II) porphyrinate and fullerene anions and between fullerene anions are simultaneously present. In these compounds, both coordination giving rise to $(Co^{II}TPP \cdot Ful^{-})$ and dimerization yielding $(Ful^{-})_2$ dimers can occur. However, since the highest unoccupied molecular orbital (HUMO) in fullerene radical anions contains only one electron, which can be involved in either coordination or dimerization, these two processes compete. This situation takes place in $(DMP^{+})_2 \cdot (C_{70}^{-})_2 \cdot$ $\cdot (Co^{II}TPP)_2 \cdot (C_6H_4Cl_2)_2$ (20). In this complex, the C_{70}^{-} radical anions undergo dimerization, whereas coordination to $Co^{II}TPP$ is absent (Fig. 20). The Co...C($(C_{70}^{-})_2$) distances are in the range of 2.753–2.804 Å and are similar to the analogous distances in the neutral Co^{II}TPP

^{*} D. V. Konarev, S. S. Khasanov, G. Saito, and R. N. Lyubovskaya, unpublished data.



Fig. 20. Fragment of the crystal structure of complex 20.⁷⁸ The $(C_{70}^{-})_2$ dimer, Co^{II}TPP, and the *N*,*N*-dimethylpyrazolium cations (DMP⁺) are shown. The shortened van der Waals Co...C($(C_{70}^{-})_2$) contacts are indicated by dashed lines.

complex with C₇₀ (2.70–2.90 Å).⁷⁴ The ESR spectrum of complex **20** (4–293 K) shows an intense asymmetric signal with $g_1 = 2.5705$ ($\Delta H = 294$ G) and $g_2 = 2.2872$ ($\Delta H = 446$ G) characteristic of Co^{II}TPP. The preferred dimerization for C₇₀ ·- radical anions is apparently attributed to higher stability of (C₇₀⁻)₂ compared to coordinatively bound {Co^{II}TPP · (C₇₀⁻)} anions.

4. Optical spectra of dimers and coordinated anions of negatively charged fullerenes

The IR spectrum of the starting C_{60} fullerene shows only four absorption bands at 527 (s), 577 (m), 1182 (m), and 1429 (s) cm⁻¹. The IR spectrum of C₇₀ fullerene has ten bands at 457 (m), 534 (s), 564 (m), 576 (s), 642 (m), 673 (m), 794 (m), 1132 (w), 1413 (w), and 1429 (s) cm⁻¹. This is due to high symmetry of the above-mentioned molecules.⁸⁹ Upon reduction to the radical-anion state, the number of bands characteristic of neutral fullerene changes only slightly, but some bands are shifted, and their intensities are redistributed. The formation of new C-C bonds in dimers leads to a lowering of the symmetry of the fullerene cage and results in the formation of a great number of new bands in the absorption spectra and splitting of the already present bands into two or three components. For example, the IR spectra of complexes containing $(C_{70})_2$ dimers show not only absorption bands belonging to donors and the solvent but also an approximately the same set of bands, which can be assigned to the dimer: 494 (w), 508 (w), 530 (s), 548 (w), 556 (w), 574 (m), 628 (w), 638 (w), 668 (m), 688 (m), 713 (w), 721 (w), 800 (s), 842 (m), 901 (w), 944 (w), 1158 (m), 1176 (w), 1210 (w), 1245 (w), 1279 (w), 1307 (w), 1323 (w), 1354 (w), 1363 (w), 1391 (s), 1412 (m), 1430 (s), 1478 (w), 1508 (w), and 1560 (w) cm^{-1} .^{46,54} These bands allow the identification of the $(C_{70}^{-})_2$ dimer in ionic complexes. Analogously, the IR spectrum of the doubly bonded $(C_{60}^{-})_2$ dimer shows a great number of new absorption bands.⁵²

The formation of coordinatively bound anions results primarily in splitting of IR-active absorption bands of fullerenes. For example, in the IR spectrum of complex **17** containing the {Co^{II}OEP · (C₆₀⁻)} anion at room temperature, the bands corresponding to the $F_{1u}(1)$ and $F_{1u}(4)$ modes of C₆₀ are split: 523 (w), 527 (w), 576 (s), 1175 (w), 1387 (s), 1395 (s), and 1398 (s) cm⁻¹.⁷⁶ However, it should be noted that an analogous splitting was observed also in the spectra of some neutral and ionic complexes containing monomeric fullerenes or their anions.^{46,99}

Coordinatively bound anions have characteristic near-IR spectra. These spectra show two absorption bands at 1092 and 1288 nm (Co^{II}TPP·C₆₀⁻),⁷⁴ 1086 and 1277 nm { $Co^{II}OEP \cdot (C_{60}^{-})$ } (Fig. 21, curve *I*),⁷⁶ 1071 and ~1210 nm ($Co^{II}TPP \cdot C_{60}(CN)_2^{-}$).^{73,74} The positions of absorption bands at 1070-1090 nm are identical to those of the individual $C_{60}{\ensuremath{\,^{-}}}$ and $C_{60}(CN)_2{\ensuremath{\,^{-}}}$ radical anions. Hence, these bands can be assigned to intramolecular transitions in fullerene anions. No absorption bands are present at 1210-1290 nm in the spectra of both the C_{60} ·- and $C_{60}(CN)_2$ ·- radical anions and porphyrins. Most likely, these bands are assigned to charge transfer between the fullerene anions and cobalt(II) porphyrinates. This assignment is proved by the absence of a band at 1210–1290 nm in the spectrum of complex 18 containing the uncoordinated (MDABCO⁺) • Co^{II}OEP and C_{60} · - fragments at room temperature (see Fig. 21, curve 3). Therefore, the formation of the Co-C coordination bond, which provides a close approach and efficient overlap between the π orbitals of the fullerene anions and cobalt(II) porphyrinates, is a necessary condi-



Fig. 21. The UV—Vis and near-IR spectra (KBr pellets, 293 K) of the {Co^{II}OEP \cdot (C₆₀⁻)} anion in complex **17** (*I*),⁷⁶ the doubly bonded (C₆₀⁻)₂ dimer in complex **11** (*2*),⁵² the {(MDABCO⁺) \cdot Co^{II}OEP \cdot (C₆₀⁻)} species in complex **18** containing uncoordinated Co^{II}OEP and C₆₀⁻ fragments (*3*),⁷⁶ and the (C₇₀⁻)₂ dimer in complex **4** (*4*).⁴⁶ The charge transfer bands are indicated by arrows.

tion for the appearance of charge transfer bands at 1210-1290 nm.

The spectrum of the doubly bonded $(C_{60}^{-})_2$ dimer shows not only two absorption bands at 905 and 1064 nm but also a new weak band at 1330 nm (see Fig. 21, curve 2).⁵² This band is absent in the spectrum of C_{60}^{-} -(940 and 1080 nm)³⁹ and can be assigned to the charge transfer band between the C_{60}^{-} anions in the dimer.

The absorption spectrum of the monomeric C_{70} - radical anion in the near-IR range shows³⁹ one band at 1363–1386 nm. Upon dimerization, the spectrum of $(C_{70}^{-})_2$ contains two broad bands at 880 and 1240 nm (see Fig. 21, curve 4).^{46,54} However, it is impossible to unambiguously determine which band (at 880 or 1240 nm) corresponds to charge transfer.

5. Formation and stability of dimers and coordinatively bound anions in ionic fullerene compounds

The synthesis and structural studies of a great number of ionic fullerene compounds demonstrated that the dimeric state is typical of fullerene radical anions (particularly, of C_{70}). In the presence of short intermolecular contacts between them, dimerization most often occurs. Complexes and salts of fullerenes with monomeric radical anions are formed more rarely and only if fullerene radical anions are rather remote from each other or isolated as a result of particular steric hindrance (due to the presence of solvent molecules and alkyl or phenyl substituents in cations). For example, the CS_2 molecules in the $Cp_2Co \cdot C_{60} \cdot CS_2$ (see Ref. 27) and $Cp_2Ni \cdot C_{60} \cdot CS_2$ complexes²⁸ are inserted between fullerene radical anions, thus hindering dimerization. In the structure of TDAE \cdot C₆₀, in spite of the presence of short C...C contacts between the C_{60} · - radical anions, dimerization does not proceed⁹ due apparently to the presence of the bulky Me substituent in the TDAE⁺⁺ radical cation. In this compound, the C_{60} ⁻ radical anions undergo polymerization^{41,42} only under a pressure of 7 kbar.

Radical recombination is the driving force of dimerization of C_{60} ⁻ radical anions.¹⁰⁰ In this case, HUMO of the C_{60}^{-} anion gives a substantial contribution to the formation of a C–C bond between the C_{60}^{-} anions in the σ dimer,¹⁰¹ which should lead to a strong electrostatic repulsion between two closely spaced negative charges. Actually, semiempirical calculations for the σ dimer $(C_{60}^{-})_2$ showed that the highest excess negative charge (-0.28 e) is located on the C atoms adjacent to the C–C bond between the fullerene fragments. However, a substantial alternation of positive and negative charges is observed in the vicinity of this bond, resulting in an increase in the distance between the charge distribution centers in the σ dimer to 9.86 Å.¹⁰¹

The factors responsible for a decrease in repulsion between two negative charges stabilize the dimeric state.

The presence of electron-deficient substituents in $C_{60}(CN)_2$, which can delocalize to a large degree the negative charge, or the more extended π system of C₇₀ fullerene compared to C₆₀ leads to an increase in the distance between the negative charges, thus stabilizing the $(C_{60}(CN)_2)_2$ and $(C_{70})_2$ dimers compared to $(C_{60})_2$. The neutral azafullerene dimer $(C_{59}N)_2$ is isoelectronic with $(C_{60})_{2}$; in the former, however, there is no repulsion between negative charges, and it is characterized by a substantially higher stability than the $(C_{60})_2 \sigma$ dimer; dissociation of this dimer begins only at temperatures higher than 500 K.¹⁰² Analogously, the dissociation enthalpies of neutral dimers formed by the RC₆₀ radicals $(R = Pr^{i}, Bu^{t}, adamantyl, CCl_{3}, P(O)(OR)_{2}, etc.)^{103-105}$ $(55-149 \text{ kJ mol}^{-1})^{103,104}$ are much higher than those of the $(C_{60}^{-})_2 \sigma$ dimers (25–63 kJ mol⁻¹).⁴⁶ An increase in the charge on the fullerene anion to 2- or 3- is responsible for an increase in repulsion between the negative charges, and dimers consisting of fullerene di- or trianions should be unstable. Apparently, this is why these dimers have not been synthesized as yet.

The starting distances between the fullerene radical anions in the monomeric phase are defined by the external environment of the dimer, *i.e.*, by cations, solvent molecules, and neutral donors involved in the complex. An increase in the distance between the centers of the C_{60} - radical anions in the monomeric phase in the series 9.986 < 10.10 < 10.124 Å (at 293 K) for $Cr(C_6H_5Me)_2 \cdot C_{60}, {}^{43,44}(Cp*_2Cr) \cdot C_{60} \cdot (C_6H_4Cl_2)_2(1), {}^{45}$ and $Cr(C_6H_3Me_3)_2 \cdot C_{60}, {}^{51}$ respectively, results in the difference in stability of the dimers and changes in their dissociation temperature (250 > 200 - 220 > below 170 K). Dimerization in the ${Cr^{I}(C_{6}H_{6})_{2}}^{\cdot+} \cdot (C_{60}^{\cdot-}) \cdot C_{6}H_{4}Cl_{2}$ complex (2) occurs in C_{60} - pairs with different distances between the centers (10.052 and 10.279 Å) giving rise to dimers, which differ in the geometric parameters and thermal stability.⁴⁷ The replacement of the solvent molecules in the complexes can lead not only to changes in the dissociation temperature of the dimers (for example, the difference between the dissociation temperatures of the $(C_{60}^{-})_2$ dimers in 2 and 3 is 80 K) but also to the formation of different fullerene structures (a polymer in $Cr(C_6H_5Me)_2 \cdot C_{60} \cdot CS_2$ ⁴⁰ and dimers in compounds 2 and 3; see Table 4).

The electronic structure of the doubly bonded $(C_{60}^{-})_2$ dimer differs from that of the diamagnetic σ dimer, because each C_{60}^{-} anion in the former dimer contains approximately one spin. This difference is associated with the different mechanisms of formation of these dimers. The doubly bonded dimer is formed by the [2+2]-cycloaddition reaction accompanied by cleavage of two π bonds in two adjacent C_{60}^{-} anions and the formation of two new C-C bonds between these anions. The electrons on HUMO of the C_{60}^{-} anions apparently remain intact. In the σ dimer, only one C-C σ bond is formed between the C_{60}^- anions, and electrons on HUMO of the C_{60}^- anion are most likely involved in its formation. A total of 61 electrons are present on the π orbitals of the starting C_{60}^- radical anion. The formation of two C—C bonds in the π dimer leads to a decrease in the number of π electrons in the C_{60}^- anion to 59, and the odd number of π electrons is responsible for paramagnetism of π dimers. The formation of one C—C bond in the σ dimer leads to a decrease in the number of π electrons in the C_{60}^- anion to 60, and the even number of π electrons gives rise to diamagnetism of σ dimers. It should be noted that the existence of two types of dimers was observed¹⁰⁶ for planar π acceptors as well, *viz.*, tetracyanoethylene and tetracyanoquinodimethane.

The electronic structures of not only dimeric but also of polymeric fullerene structures depend both on the charge on the fullerene anion and the number of the C–C bonds that formed. For example, the linear $(C_{60})_x$ polymer (in which each C_{60}^{-} anion forms four C-C bonds) (see Fig. 1, a) or the polymer formed by the $(C_{60}^{3-})_x$ trianions (in which each C_{60}^{3-} anion forms two C–C bonds) should retain an odd number of π electrons $(61 - 4 = 57 \text{ and } 63 - 2 = 61 \pi \text{ electrons, respectively})$ and be paramagnetic. Actually, these polymers are characterized by temperature-independent paramagnetism associated with their metallic conductivity.^{11-13,16,17} The $(C_{70}^{2-})_x$ polymer formed by dianions (in which each C_{70}^{2-} anion forms two C-C bonds) or the two-dimensional polymer $(C_{60}^{4-})_x$ (in which each C_{60}^{4-} anion forms four new C-C bonds) should contain an even number of π electrons (72 - 2 = 70 and 64 - 4 = 60 π electrons, respectively) and be diamagnetic.

A dense packing of fullerene anions in ionic fullerene compounds is a necessary condition for the appearance of high conductivity or magnetic ordering. In this case, dimerization is an unfavorable factor because it gives rise to diamagnetic species in compounds. However, since dimerization is reversible, for example, under exposure to light, the transition from the dimeric diamagnetic state to the monomeric paramagnetic state can occur. In future, this phenomenon can find use in the design of switches or data recording devices.

The formation of Co–C coordination bonds has the same nature as dimerization. Electrons from HUMO of fullerene radical anions and the d_{z2} orbitals of cobalt(II) porphyrinate are involved in the formation of these bonds. Neutral fullerenes with vacant HUMO do not form such bonds. The formation of the Co–C coordination bond leads to pairing of electrons of Co^{II}TPP and fullerene radical anions, and the resulting {Co^{II}Porph•(Ful⁻)} anions become diamagnetic. It should be noted that the electron of the C₆₀⁻ anion is to a considerable extent retained on the fullerene cage because the charge state of C₆₀ in complexes **13** and **17** containing coordinatively bound anions is close to 1– (IR spectroscopic data).^{74,76}

The {Co^{II}Porph \cdot (C₆₀⁻)} anions are more stable than the corresponding $(C_{60}^{-})_2$ dimers because there is no repulsion between negative charges in these anions. Destabilization of $Co-C(C_{60}^{-})$ bonds can be caused by additional coordination of the Co atom by the nitrogen-containing ligand, which approaches from the opposite side (relative to the C_{60}^{-} anion) of the porphyrin macrocycle, and the Co atom is pulled closer to this ligand (see Fig. 17, a). In this case, the unusual diamagnetic-paramagnetic transition from the coordinated state with paired electrons of Co^{II} porphyrinate and C_{60}^{-} to uncoordinated paramagnetic species is observed. The transitions associated with dissociation of Co-C coordination bonds are very broad (~200 K) and are, most likely, not caused by structural phase transitions, as opposed to dissociation of dimers (the structural transition upon dimerization was not observed only in $Cr^{I}(C_{6}H_{3}Me_{3})_{2} \cdot C_{60}$.⁵¹

The fullerene radical anions containing one electron on HUMO (π^{*1}) are similar to the NO molecule, which also contains one electron on HUMO (π^{*1}), and can be considered as one-electron ligands. It should be noted that the coordinatively bound Co^{II}TPP•NO species, whose electronic configuration is similar to that of {Co^{II}TPP•(C₆₀⁻)}, is also diamagnetic and gives no ESR signals.¹⁰⁷ The fullerene dianions can be considered as two-electron ligands, which are analogous to the O₂ molecule containing two electrons on HUMO (π^{*2}) and forming the paramagnetic Co^{II}TPP•O₂ species.¹⁰⁷

The chemistry of ionic fullerene compounds is a new extensively developed line of investigation, which involves the synthesis and studies of the properties of compounds containing fullerene radical anions in different oxidation states.

Studies of compounds with dimeric, polymeric, and coordinatively bound fullerene anions is an important part of these investigations and hold promise both from the fundamental viewpoint and for the design of new materials. We developed methods and approaches, which provide wide possibilities for synthesizing new ionic fullerene compounds. It is known that fullerenes form stable anions with charge states up to 6–. For most of these compounds, new dimeric, polymeric, or coordination structures can be synthesized.

The reversible C–C bond formation and coordination giving rise to M–C bonds have a substantial effect on the electronic structures of fullerenes and, consequently, on the conducting, magnetic, and optical properties of ionic compounds. In compounds containing spins on dimers, polymers, or coordination structures, the metallic conductivity (probably, superconductivity) and magnetic ordering of spins would be expected to exist. For example, a strong antiferromagnetic interaction between spins with the Weiss constant of -36 K is observed in complex **11** containing the paramagnetic doubly bonded $(C_{60}^{-})_2$ dimer. Not only spins located on the dimer but also spins located on cobalt(II) porphyrinates are involved in magnetic interactions, and these interactions are transferred through the $(C_{60}^{-})_2$ dimer⁷⁶

In future, we plan to synthesize and study ionic compounds containing fullerene anions with a charge of 2- and 3- and study the structures and properties of dimers, polymers, and related coordinatively bound anions. We also plan to prepare ionic compounds with porphyrinates of such metals, as Fe^{II} and Mn^{II}, to which fullerene radical anions can be coordinated under particular conditions. In this case, paramagnetic coordinatively bound anions characterized by different types of magnetic interactions would be expected to be generated.

This study was financially supported by the Russian Science Support Fellowship, the INTAS Fellowship Grant for Young Scientists (Grant YSF 05-109-4653), and the Russian Foundation for Basic Research (Project Nos 06-03-32824 and 06-03-91361).

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Received December 13, 2006; in revised form March 2, 2007