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New approaches to the synthesis of transition-metal complexes of fullerenes C_{60} and C_{70} †

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The most important fields of coordination chemistry of fullerenes, including those dealing with synthesis and properties of η^2 complexes, multinuclear complexes and coordination dimers, have been considered. In addition, our recent results have been presented concerning the synthesis of fullerene complexes with transition metals by the reduction method and through the reaction of transition-metal compounds with fullerene radical anion salts. The properties of coordination compounds with monomeric, dimeric and polymeric fullerenes as well as with fullerene anions are discussed.
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I. Introduction

Fullerene C_{60} (Ref. 1) can form different complexes with transition metals (iridium, palladium, platinum, ruthenium, rhodium, osmium, chromium, titanium and some others).[2–5] In the simplest case, these complexes form through the dihapto coordination of metal atoms to a C–C bond at a 6:6 ring junction of the C_{60} molecule (η^2 coordination). Other types of coordination of transition metals to fullerene C_{60} are also theoretically possible,[6] and some of them have been realized.[7,8] To date, several tens of fullerene complexes have been synthesized. In most of these compounds, fullerenes are monomeric and act as neutral ligands, and the metal atoms are, as a rule, diamagnetic.[3–5]

Transition-metal complexes with fullerenes are of interest for the design of conducting, magnetic and optically active materials. In particular, fullerene complexes with paramagnetic metals can be molecular magnets in which the coordinated metal atoms have a spin, while fullerene is able to transfer magnetic interaction between these spins. An essential condition for the realization of these properties is electron density transfer from the metal atom to fullerene to form a fullerene anion or radical anion. The presence of the spin on the fullerene anion can lead to the appearance of conductivity and significantly enhance magnetic exchange between paramagnetic metal atoms coordinated to fullerene. Metal–fullerene complexes can be catalysts and nonlinear optical materials. Some of coordination compounds stable in the course of reduction and strongly absorbing in the visible region can be used, like chemically modified fullerenes, for the design of photovoltaic devices.[9]

An important and fascinating challenge for the coordination chemistry of fullerenes is to create dimeric and polymeric fullerene structures. It is well known that spin-bearing fullerene polymers can exhibit metallic conductivity and even superconductivity.[10–12] The number of possible anionic fullerene polymers is rather high: they can be linear or zigzag chains of two-dimensional polymers of different geometry.[13–17] Charge transfer in coordination polymers of fullerene that have paramagnetic centres can lead to the appearance of unique conducting and magnetic properties.

Among the known methods of synthesis of fullerene complexes are the substitution of ligands in the metal coordination sphere and the addition of fullerenes to coordinatively unsaturated metal atoms or even clusters,

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e.g., Ir_4, Rh_6 and others. Fullerene complexes have been comprehensively reviewed by Balch and Olmstead, Park and other researchers.[3–5]

Synthesis of molecular complexes and radical anion compounds of fullerenes has for a long time been an object of interest to researchers at the Institute of Problems of Chemical Physics of the RAS. Methods of synthesis of different classes of fullerene compounds in the crystalline form have been developed, which makes it possible to study their structure and properties in detail.[18–20] Fullerene reduction can also be successfully used for producing fullerene complexes with transition metals.[21–30]

Research is carried out in several directions: (1) synthesis of complexes with paramagnetic metals, for example, zero-oxidation-state cobalt with the d^9 electronic configuration and spin $S = 1/2$;[26] (2) synthesis of fullerene dimers and even polymers bonded through metal atoms;[24, 25, 27, 28] (3) synthesis of coordination compounds with fullerene anions and radical anions.[29, 30] The present review focuses precisely on these aspects of the coordination chemistry of fullerenes. In the first part of the review, we discuss the most important trends of the coordination chemistry of fullerenes, methods of synthesis of fullerene complexes and their molecular structures. In the second part of the review, we present the results of our recent studies.

II. Fullerene complexes

II.1. Fullerenes

Fullerene C_{60} — an allotrope of carbon — was discovered in 1985.[1] The structure of C_{60} consists of 60 identical carbon atoms involved in two types of C–C bonds. Short bonds at the 6:6 ring junctions (6:6 bonds) with a length of 1.38 Å are similar in chemical properties to the double bond in alkenes and are most reactive in coordination to metal atoms. The fullerene ligands behave as electron-deficient alkenes, such as tetracyanoethylene. The C–C bonds at the junction of a hexagon and a pentagon in C_{60} (6:5 bonds) are longer (1.45 Å) and less reactive. Great interest in fullerene was aroused after 1990, when the synthesis of fullerene in gram amounts was developed and its isolation in the individual state was described.[31]

In addition to fullerene C_{60}, there are higher fullerenes, for example, C_{70}, C_{76}, C_{78} and C_{84}. Fullerene C_{70} with symmetry D_{5h} is the most available compound among the higher fullerenes. As distinct from C_{60}, it contains five types of carbon atoms involved in C–C bonds of eight types. The bonds of four types at the 6:5 ring junctions are longer and, as a rule, are not involved in coordination. The bonds of the other four types at the 6:6 ring junctions are shorter and can be involved in coordination of transition-metal atoms. For two of these bonds (designated as *a*–*b* and *c*–*c*), the highest π-bond order (0.58–0.60) has been calculated;[32] as a rule, it is precisely such bonds that are more active in coordination.

Transition-metal compounds with fullerenes can be formally divided into two large families: endohedral (the metal atom is inside the fullerene cage but is not involved in coordination)[33, 34] and exohedral in which the metal atom is coordinated to the fullerene sphere. In such compounds, fullerene acts as an electron-deficient alkene ligand, and metal ions coordinate to them in an η^2-fashion or other types of coordination.[2, 3] In this review, we consider only exohedral fullerene compounds.

An important feature of fullerene chemistry is their high acceptor ability. In particular, fullerenes C_{60} and C_{70} are reversibly reduced even at −0.49 and −0.48 V against the saturated calomel electrode (SCE) in an acetonitrile–toluene mixture; under the same conditions, the second reduction potential of these fullerenes is −0.88 and −0.85 V, respectively.[35] Salts and charge-transfer complexes based on fullerene anions can exhibit interesting physical properties, including high conductivity and magnetic spin ordering. Such fullerene compounds have been considered in review.[20] The possibility to obtain fullerene anions in different charge and spin states considerably enlarges the range of fullerene complexes since not only neutral fullerenes but also their radical anions and dianions can form coordination compounds.

It is currently known that fullerenes, both as neutral molecules and anions, can dimerize or polymerize through the [2+2]-cycloaddition reaction involving the cleavage of two π-bonds in the molecules and formation of two σ-bonds between the cages.[6–8, 12, 13, 36–39] In addition, dimerization and polymerization of fullerene anions can occur through the formation of one σ-bond between the molecules.[13–17, 40–43] The ability to dimerize and polymerize provides additional tools for molecular design of fullerene complexes.

II.2. Dihapto coordination of fullerenes to transition metals

The $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$ complex, in which fullerene C_{60} was used as a ligand for the first time, was synthesized in 1991 (Fig. 1 *a*).[44, 45] In following years, numerous transition-metal complexes have been synthesized not only with C_{60}, but also with higher fullerenes C_{70} and C_{84}. For example, the reaction of $(Ph_3P)_2Rh(H)(CO)$ or $(Ph_3P)_2Pd(\eta^2\text{-}C_2H_4)$ with C_{70} gives the $(Ph_3P)_2Pd(\eta^2\text{-}C_{70})$[46] and $(Ph_3P)_2Rh(H)(CO)(\eta^2\text{-}C_{70})$[47] complexes (see Fig. 1 *b*), and the triphenylphosphine iridium complex $(Ph_3P)_2IrCl(CO)$ reacts with fullerene C_{84} to give $(Ph_3P)_2IrCl(CO)(\eta^2\text{-}C_{84})$.[48]

Many transition-metal complexes with η^2-coordination are synthesized by the substitution reaction; for example,

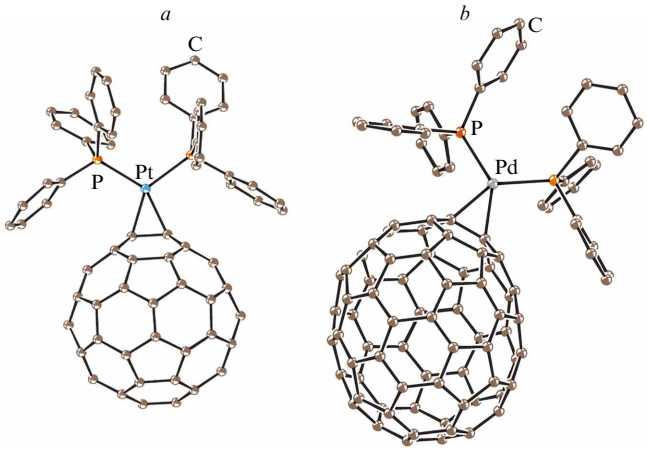


Figure 1. Molecular structures of the fullerene C_{60} complex with bis(triphenylphosphine)platinum(0) $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$ (*a*)[44, 45] and the fullerene C_{70} complex with bis(triphenylphosphine)palladium(0) $(Ph_3P)_2Pd(\eta^2\text{-}C_{70})$ (*b*).[46]

$(\eta^5\text{-Cp})_2TaH(\eta^2\text{-}C_{60})$ (Cp = C_5H_5) has been synthesized by the reaction of C_{60} with $(\eta^5\text{-Cp})_2TaH_3$ in benzene.[49] Photolysis of $(dppe)W(CO)_4$ [dppe is 1,2-bis(diphenylphosphino)ethane] or $(PhMe)Cr(CO)_3$ in the presence of C_{60} leads to the $(dppe)W(CO)_3(\eta^2\text{-}C_{60})$ or $(PhMe)Cr(CO)_2(\eta^2\text{-}C_{60})$ complexes.[50, 51] Platinum, palladium and nickel complexes $L_2M(\eta^2\text{-}C_{60})$, where L is a monodentate or bidentate phosphine, are usually synthesized through the substitution of fullerene for one or two ligands in the metal coordination sphere [reactions (1), (2)].[44, 52]

$$(Ph_3P)_2M(\eta^2\text{-}C_2H_4) + C_{60} \longrightarrow (Ph_3P)_2M(\eta^2\text{-}C_{60}) + C_2H_4 \quad (1)$$

M = Pt, Pd

$$(R_3P)_4M + C_{60} \longrightarrow (R_3P)_2M(\eta^2\text{-}C_{60}) + 2\,R_3P \quad (2)$$

M = Pt, Pd, Ni; R = Et, Ph

Iridium and rhodium form complexes with fullerenes coordinated in an η^2-fashion, L_nMC_{60} and L_nMC_{70}, where n is commonly 4, but can also be 3. The coordination sphere is completed with phosphine, halide and carbonyl ligands. In particular, interdiffusion of concentrated solutions of C_{60} and $(PPh_3)_2IrCl(CO)$ in benzene leads to the formation of black crystals of $(PPh_3)_2IrCl(CO)(\eta^2\text{-}C_{60})$, structurally characterized by X-ray crystallography.[53] Analogous complexes have been synthesized with higher fullerenes[48] and iridium compounds containing other tri(alkyl,aryl)phosphine ligands.[54] In all these reactions, fullerene is either substituted for ligands at the metal atom (H_2, CO, C_2H_4, Et_3P, Ph_3P) or added to coordinatively unsaturated metal atoms, such as iridium or rhodium with coordination number (C.N.) four.

Common features of such fullerene C_{60} complexes can be considered using $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$ as an example.[44, 45] The length of the C – C bond at the 6 : 6 ring junction in fullerene to which the platinum atom is coordinated is 1.502(30) Å, which considerably exceeds the average length of the 6 : 6 bonds in the C_{60} molecule not involved in coordination [1.388(30) Å]. The Pt – C(C_{60}) bond lengths are 2.145(24) and 2.115(23) Å, which is close to similar bond lengths in the complex with ethylene $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$, 2.106(4) and 2.116(9) Å.[55] When the metal atom is coordinated to a π-bond of the fullerene, the carbon atoms involved in this bond leave the fullerene sphere so that pyramidalization of the carbon atoms bonded to the Pt atom occurs (the pyramidalization angle is 15.4°, which noticeably exceeds the angle 11.64° typical of fullerene C_{60}).[56]

Studying the electrochemical properties of $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$[57] and a series of $\{(Et_3P)_2Pt\}_n(\eta^2\text{-}C_{60})$ compounds (n = 1 – 4)[58] has shown that they can be reduced to a trianion with insignificant dissociation into the corresponding fullerene anion and a metal-containing fragment. For $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$, the first reduction potential is shifted by 0.3 V toward more negative values with respect to C_{60};[57] for the $\{(Et_3P)_2Pt\}_n(\eta^2\text{-}C_{60})$ compounds (n = 1 – 4), the addition of each metal atom to fullerene is accompanied by the shift of the first reduction potential with formation of a monoanion by ~0.36 V toward negative values.[58] Thus, the fullerene complexes are significantly weaker acceptors than the fullerenes themselves.

In the Raman spectra of $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$, high-frequency absorption bands of C_{60} are shifted toward lower frequencies and new absorption bands appear because of the lowering of the symmetry of C_{60} upon coordination.[59] The shift of absorption bands reflects the weakening of the C – C bonds in fullerene and is consistent with X-ray crystallographic data. This effect as well as the elongation of the bond at the 6 : 6 ring junctions involved in coordination can be associated with back electron density transfer from the occupied d orbital of the metal to the vacant antibonding π* orbital of C_{60} (d – π back donation).[2]

In general, a significant shift of reduction potentials of $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$ toward negative values can indicate an increase in the electron density on the fullerene upon coordination to a metal atom. However, in most of the known fullerene complexes, including $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$, the metal – fullerene charge transfer is insignificant, and the charge state of fullerenes in these compounds is close to zero. At the same time, it is well known that the filling of the lowest unoccupied molecular orbital (LUMO) of C_{60} leads to the appearance of new absorption bands in the near-IR range at 940 – 960 and 1060 – 1080 nm related to electron transitions from the LUMO of C_{60}^- to higher-lying orbitals.[20] Thus, the generation of the fullerene anion is reliably detected in the near-IR spectra. The appearance of an unpaired electron on C_{60} should lead to the appearance of a characteristic signal in the EPR spectrum with the g value in the range 2.000 – 1.996,[20] which is evidence of the formation of the fullerene radical anion. However, none of the known fullerene complexes gives rise to the bands in the near-IR range with respect to C_{60}^- and even more so to the EPR signal due to the $C_{60}^{-\bullet}$ radical anion.[2, 3]

II.3. Multinuclear transition-metal complexes

Most of the transition metals form mononuclear complexes with fullerenes. The first multinuclear complexes of C_{60} were synthesized by the reaction of fullerene with an excess of $(Et_3P)_4M$ (M = Pt, Pd). The hexa-substituted fullerene derivative was synthesized as a single isomer and characterized by X-ray crystallography (Fig. 2 *a*). The six platinum atoms are coordinated to the C – C bonds at the 6 : 6 ring junctions to form an octahedral array around the fullerene cage. The symmetry of the $C_{60}Pt_6P_{12}$ core is close to ideal symmetry T_h. Spectroscopic methods have shown that the hexa-adduct forms through $\{(Et_3P)_2Pt\}_nC_{60}$ intermediates (n = 2 – 5), and their structural characterization failed.[60]

Fullerene can coordinate to four metal-containing species. In particular, the reaction of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with fullerene C_{70} gives four products $(Ph_3P)_2Pt\}_nC_{70}$ (n = 1 – 4). The compound with n = 4 has been isolated as crystals, and it has been characterized by X-ray crystallography (see Fig. 2 *b*).[61]

Binuclear complexes with $\mu\text{-}\eta^2,\eta^2\text{-}C_{60}$ coordination mode are typical of rhenium, for example, $(Me_3P)_4Re_2H_8(\eta^2,\eta^2\text{-}C_{60})$,[63] ruthenium — $(\eta^5\text{-Cp*})_2Ru_2.(\mu\text{-Cl})(\mu\text{-X})(\eta^2,\eta^2\text{-}C_{60})$ (X = H, Cl; Cp* = C_5Me_5)[64] and iridium — $\{Ir_2Cl_2(\eta^4\text{-cod})_2\}_2(\eta^2,\eta^2\text{-}C_{60})$[65] (cod is 1,5-cyclooctadiene) and $\{(Me_2PhP)_2IrCl(CO)\}_2(\eta^2,\eta^2\text{-}C_{60})$[62] (see Fig. 2 *c*).

Coordination of several paramagnetic metal atoms to the fullerene cage can lead to magnetic compounds in which magnetic exchange between paramagnetic centres can occur through the fullerene molecule or its anion.

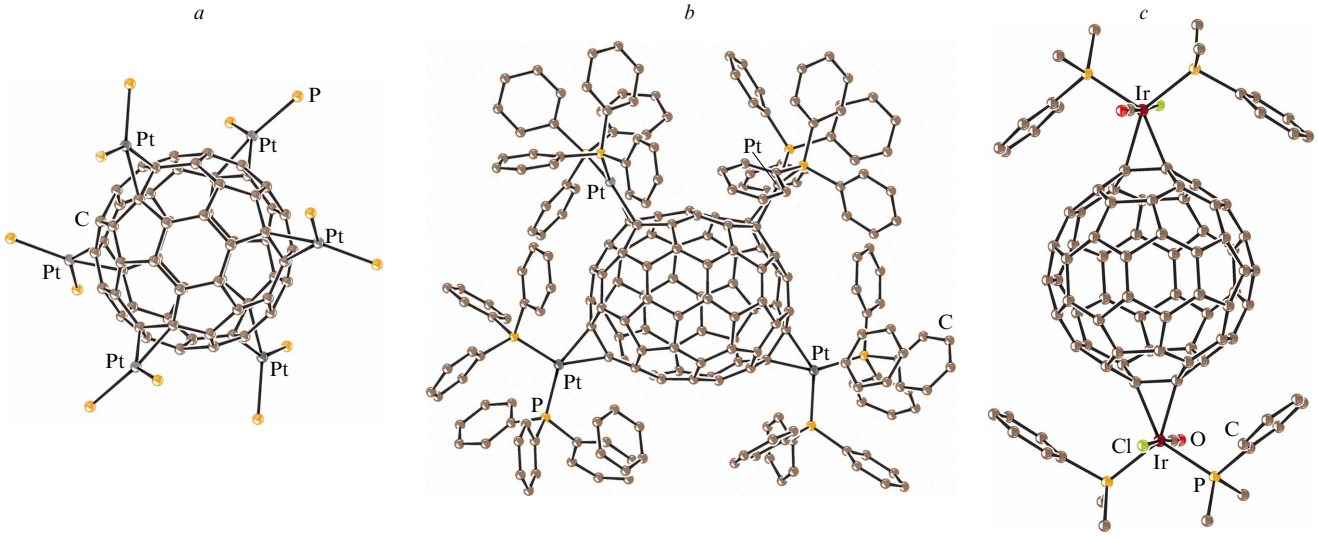


Figure 2. Molecular structures of multinuclear transition-metal complexes with fullerenes.
(*a*) Hexanuclear complex (μ_6-$\eta^2,\eta^2,\eta^2,\eta^2,\eta^2,\eta^2$-$C_{60}$-fullerene)hexakis{bis(triethylphosphine)platinum} (the ethyl substituents of triethylphosphine are not shown for simplicity);[60] (*b*) tetranuclear complex (μ_4-$\eta^2,\eta^2,\eta^2,\eta^2$-$C_{70}$-fullerene)tetrakis{bis(triphenylphosphine)platinum};[61] (*c*) binuclear complex (μ-η^2,η^2-C_{60}-fullerene)bis{carbonyl(chloro)bis(dimethylphenylphosphine)iridium}.[62]

II.4. Other types of coordination of metal atoms to the fullerene C_{60} molecule

In most of the above complexes, the metal atoms are coordinated to two carbon atoms of fullerene. A less common coordination mode is to five or six carbon atoms of fullerene. For example, in the ruthenium complex $Ru_3(CO)_9(\mu_3$-η^2,η^2,η^2-$C_{60})$ (Fig. 3 *a*), each metal atom is coordinated to a separate pair of carbon atoms in one hexagon of fullerene (μ_3-η^2,η^2,η^2-bonding).[7] In complexes with the $C_{60}Me_5^-$ ligand, the metal coordinates in an η^5 fashion to a pentagon of the fullerene, which acts as a cyclopentadienyl ligand with several substituents. The $(CpFe)(\eta^5$-$C_{60}Me_5)$ complex (see Fig. 3 *b*) has a similar type of bonding as in ferrocene where one cyclopentadienyl ligand is replaced by the $C_{60}Me_5^-$ anion.[8]

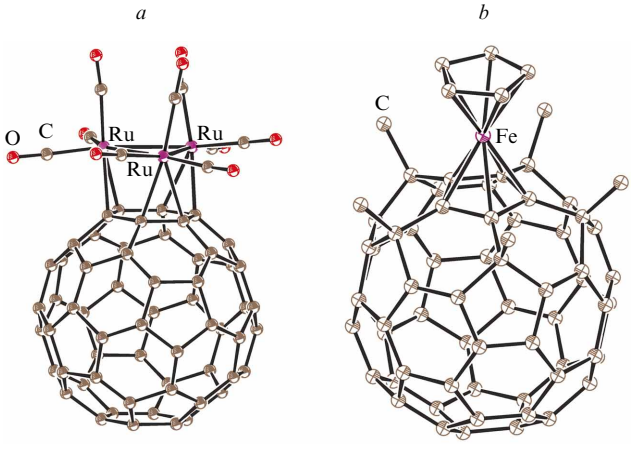


Figure 3. Coordination of the $Ru_3(CO)_9$ moiety to fullerene C_{60} in a μ_3-η^2,η^2,η^2 fashion (*a*)[7] and η^5-coordination of the $C_{60}Me_5^-$ ligand to the η^5-CpFe moiety (*b*).[8]

II.5. Dimeric transition-metal complexes with fullerene C_{60}

Most transition metals form only monomeric complexes with fullerene C_{60}. However, acting like bridges, atoms or even clusters of some metals can be coordinated to two C_{60} molecules, which leads to the formation of coordination dimers.

To date, several coordination dimers of fullerene C_{60} have been synthesized. In particular, tungsten(0) and molybdenum(0) surrounded by carbonyl ligands and 4,4′-di(*n*-butoxycarbonyl)-2,2′-bipyridine (dbcbipy) are coordinated in an η^2 fashion to 6:6 bonds of two C_{60} molecules to form $(dbcbipy)M(CO)_2(\eta^2$-$C_{60})_2$ (M = W, Mo) (Fig. 4 *a*). The coordination environment of the metal atom comprises eight atoms. Two CO groups and bipyridine are located in the equatorial plane.[66]

Coordination dimers of fullerene can form when diphosphine ligands act as bridges between two metal atoms coordinated to fullerene, like in $Pd_2(\mu$-*trans*-$dppe)_2(\eta^2$-$C_{60})$ (see Fig. 4 *b*). The distance between the fullerene cage centres is 17.95 Å;[67] *i.e.*, a large size of the diphosphine ligand is responsible for the large distances between the fullerenes in such dimers.

The reaction of the $(Me_3P)_4Ir_4(CO)_8$ cluster with a C_{60} excess in boiling *o*-dichlorobenzene in the presence of CNR (R = Bn) gives the fullerene complex with iridium $(Me_3P)_2Ir_4(CO)_3(\mu_4$-$CH)(\mu$-$Me_2P)(CNR)(\mu$-$\eta^2,\eta^2$-$C_{60})$. $.(\mu_4$-$\eta^1,\eta^1,\eta^2,\eta^2$-$C_{60})$. In this complex, two iridium atoms from the Ir_4 cluster are bonded to two C_{60} molecules, while the other two iridium atoms are bonded only to one fullerene. As a result, two fullerenes in the dimer have different coordination modes, μ-η^2,η^2 and μ_4-$\eta^1,\eta^1,\eta^2,\eta^2$ (see Fig. 4 *c*).[68]

The reaction of the monomeric fullerene complex with the rhodium cluster $(dppm)_2Rh_6(CO)_9(\mu_3$-η^2,η^2,η^2-$C_{60})$ [dppm is bis(diphenylphosphino)methane] with the second C_{60} equivalent and subsequent treatment of the reaction product with CNR (R = Bn) leads to the coordination dimer $(dppm)_2Rh_6(CO)_5(CNR)(\mu_3$-$\eta^2,\eta^2,\eta^2$-$C_{60})_2$, in

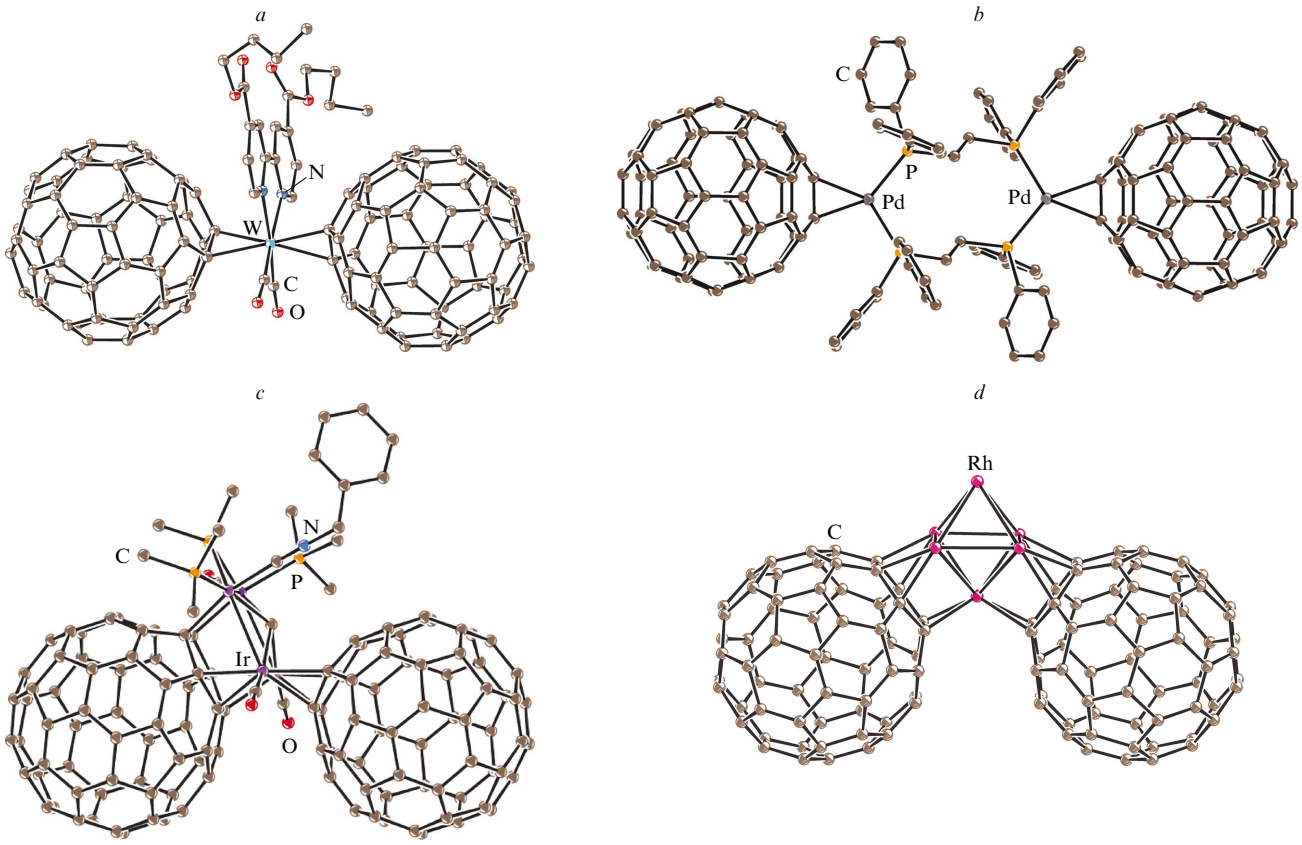


Figure 4. Molecular structures of coordination dimers (dbcbipy)W(CO)$_2$(η^2-C$_{60}$)$_2$ (*a*),[66] Pd$_2$(μ-*trans*-dppe)$_2$(η^2-C$_{60}$)$_2$ (*b*),[67] (Me$_3$P)$_2$Ir$_4$(-CO)$_3$(μ$_4$-CH)(μ-Me$_2$P)(CNBn)(μ-η^2,η^2-C$_{60}$)(μ$_4$-η^1,η^1,η^2,η^2-C$_{60}$) (*c*) [68] and (dppm)$_2$Rh$_6$(CO)$_5$(CNBn)(μ$_3$-η^2,η^2,η^2-C$_{60}$)$_2$ (*d*) (for simplicity, the Rh$_6$ cluster is shown without additional ligands).[69]

which two fullerene molecules are linked through the cluster of six rhodium atoms (see Fig. 4 *d*).[69]

The distances between the fullerene C$_{60}$ centres and the length of C···C contacts in the coordination dimers are, respectively, 10.29 and 3.25 Å in (Me$_3$P)$_2$Ir$_4$(CO)$_3$.(μ$_4$-CH)(μ-Me$_2$P)(CNR)(μ-η^2,η^2-C$_{60}$)(μ$_4$-η^1,η^1,η^2,η^2-C$_{60}$) (R = Bn),[68] 10.34 and 3.59 Å in (dppm)$_2$Rh$_6$(CO)$_5$.(CNR)(μ$_3$-η^2,η^2,η^2-C$_{60}$)$_2$,[69] and 11.58 and 4.39 Å in (dbcbipy)M(CO)$_2$(η^2-C$_{60}$)$_2$.[66] Taking into account that the van der Waals radius of the C$_{60}$ molecule is 10.18 Å, we can conclude that the fullerene molecules in these dimers are not closely packed.

Available literature data show that there are no special methods of synthesis of coordination dimers and, even more so, fullerene polymers formed through metal bridges. At the same time, the development of new methods of their synthesis is an important task. Synthesis of such complexes with paramagnetic metals and the increase in the degree of charge transfer from the metal to the fullerene molecule can lead to strong magnetic interactions. That is especially important since the dimeric structures where triplet states can be generated by interaction of spins localized on fullerene radical anions, as is observed in the $(C_{60}^{-})_2$ dimer formed through two C–C bonds.[39] An analogous situation can occur when a dimer is formed through two bridging paramagnetic metal atoms. It is also known that the presence of two fullerene cages in the same molecule leads to a nonlinear increase in polarizability of fullerenes C$_{60}$,[70] C$_{70}$ and some other fullerenes;[71, 72] in addition, calculations predict the increase in hyperpolarizability of fullerenes in the dimeric state.[73]

III. Synthesis of coordination compounds by the reduction of metal salts in the presence of fullerenes

It is known that zero-oxidation-state metals are most active for coordination.[2, 3] Therefore, we have developed methods of metal reduction in the presence of fullerenes, which enable the synthesis of transition-metal complexes with fullerenes.

Initial reagents were compounds of doubly charged metals M^{II}(L)X$_2$ [M = Ni, Co; X = Cl, Br; L is a phosphine or diphosphine ligand, including Ph$_3$P, Me$_3$P, dppe, 1,3-bis(diphenylphosphino)propane (dppp), 1,1′-bis(diphenylphosphino)ferrocene (dppf)]. The M^{II}(L)X$_2$ compounds are produced by the reaction of metal chlorides or bromides with corresponding phosphines or diphosphines in acetonitrile; they precipitate from acetonitrile in the course of reaction or crystallize upon removal of the solvent.

The metals in M^{II}(L)X$_2$ can be reduced by different reducing agents. For example, the strong single-electron reducing agent sodium fluorenone ketyl (oxidation potential $E^{-/0} = -1.17$ V *vs.* SCE) [74] can readily reduce nickel and cobalt salts in the presence of fullerenes to form coordination compounds.

On heating in *o*-dichlorobenzene, a zinc powder generates nickel complexes, while cobalt compounds are formed only in low yield. This is explained by a relatively low

oxidation potential of zinc (−0.76 V vs. SCE),[75] which is insufficient for reducing cobalt to the zero oxidation state. The addition of fluorenone ketyl can significantly increase the yield of the cobalt complex. Nickel complexes can be synthesized by using two equivalents of sodium tetraphenylborate, but its potential is insufficient for the synthesis of cobalt compounds. More exotic reducing agents can also be used for reduction, for example, chromium acetylacetonate $Cr^{II}(acac)_2$, which has an oxidation potential of −1.47 V *vs.* SCE.[76]

III.1. Nickel complexes with fullerenes C_{60} and C_{70}

The formation of nickel(0) complexes with C_{60} in the presence of a reducing agent (Red) can be represented by reaction (3).

$$Ni^{II}(L)Cl_2 + C_{60} + 2\,Red \longrightarrow Ni^{0}(L)(\eta^2\text{-}C_{60}) \quad (3)$$

Red = $NaBPh_4$, Zn, fluorenone ketyl; L = Me_3P, dppe, dppp, dppf

If the reaction is carried out in stages, the complexes can be obtained in lower yields: first, the nickel compound $Ni^{II}(L)Cl_2$ is reduced with two equivalents of a reducing agent, and then, neutral fullerene is added [reaction (4)]; or first, a radical anion C_{60} salt is obtained in a solution, and then, the corresponding nickel compound $Ni(L)Cl_2$ is added [reaction (5)].

$$Ni^{II}(L)Cl_2 + 2\,Red \longrightarrow Ni^{0}(L) \xrightarrow{C_{60}} Ni^{0}(L)(\eta^2\text{-}C_{60}) \quad (4)$$

$$C_{60} + Red + Cat^{+}Cl^{-} \longrightarrow Cat^{+}(C_{60}^{-\bullet}) \xrightarrow{Ni(L)Cl_2} Ni^{0}(L)(\eta^2\text{-}C_{60}) \quad (5)$$

The method that we developed for the synthesis of coordination compounds through the reduction of metal salts was tested for the nickel compounds with diphosphine ligands (dppe, dppp and dppf). The reduction of $Ni^{II}(L)Cl_2$ and fullerene leads to the formation of green solutions for C_{60} and red-brown solutions for C_{70}. Slow diffusion of hexane into these solutions leads to the formation of crystals of $Ni(dppp)(\eta^2\text{-}C_{60})\cdot 0.84\,C_6H_{14}\cdot 0.16\,C_6H_4Cl_2$ (**1**), $Ni(dppe)(\eta^2\text{-}C_{60})\cdot C_6H_4Cl_2$ (**2**), $Ni(dppf)(\eta^2\text{-}C_{60})\cdot 0.5\,C_6H_4Cl_2\cdot 0.5\,C_6H_{14}$ (**3**) and $Ni(dppp)(\eta^2\text{-}C_{70})\cdot 0.5\,C_6H_4Cl_2$ (**4**) ($C_6H_4Cl_2$ is *o*-dichlorobenzene).[21–23] In all cases, the metal atom is coordinated to a 6:6-bond of C_{60} or to an *a*–*b* bond shared by two hexagons of C_{70} (Fig. 5 *a*,*b*), and the latter has one of the highest π-bond orders in C_{70}. In these complexes, the nickel atom has a roughly square-planar environment. The Ni–C bond length is within 1.936(6)–1.977(3) Å for C_{60} (Table 1) and 1.929(2)–1.941(2) Å for C_{70}. These are the shortest metal–carbon bonds observed in fullerene complexes. The Ni–C(C_{60}) bond length depends on the diphosphine used. The increase in the P–Ni–P angle in the Ni(L) moiety leads to the elongation of the Ni–C(C_{60}) bond (see Table 1). The C–C bonds of C_{60} and C_{70} molecules involved in coordination are significantly elongated from the average values 1.381(9)–1.389(4) Å to 1.475(8)–1.494(2) Å. Such an elongation can be associated with electron density transfer from the occupied d orbitals of the nickel atom to the vacant antibonding π* orbitals of fullerenes.

The spectra of C_{60} complexes in the IR range show the softening and splitting of the $F_{1u}(4)$ mode of C_{60} sensitive to charge transfer to the molecule and to the change in its symmetry.[77,78] The $F_{1u}(4)$ mode of C_{60} is observed at 1429 cm^{-1} in the spectrum of neutral fullerene C_{60}, at 1388–1396 cm^{-1} in the spectra of radical anion salts[20] and at 1412–1420 cm^{-1} in the spectra of fullerene complexes.[21,23–30] Analysis of spectral data demonstrates that the spectra of solid compounds **1**–**4** and their solutions show no absorption bands in the near-IR range that could be assigned to fullerene anions. The EPR spectra show only narrow impurity signals with the intensity not exceeding 2% of the total fullerene content. These data are indicative of the neutral state of fullerenes in complexes **1**–**4**. Despite the neutral character, the nickel complexes of fullerenes are

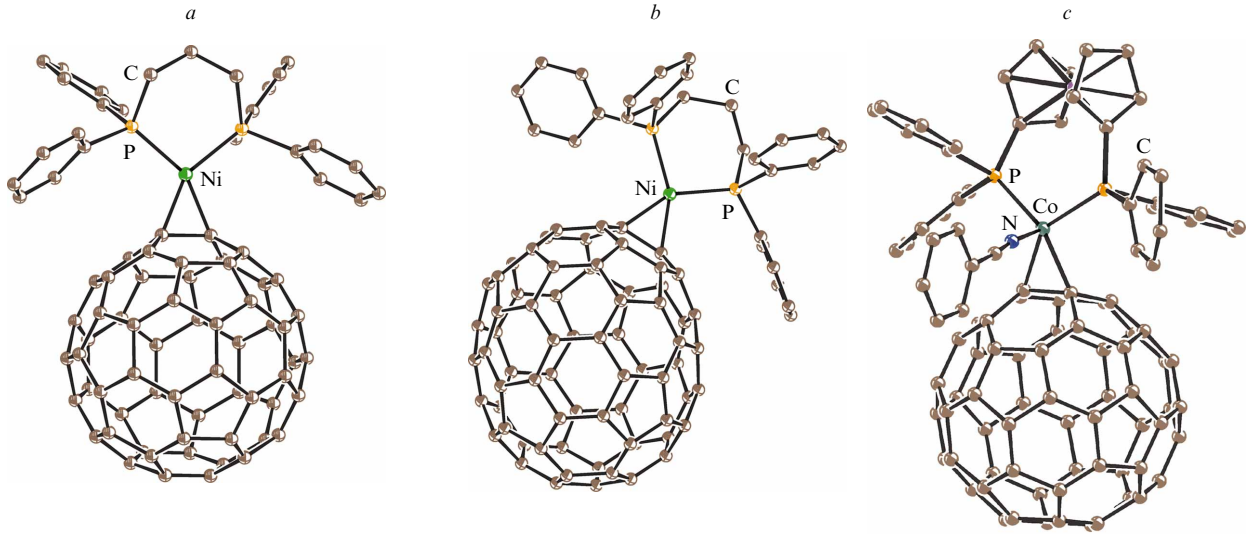


Figure 5. Structures of Ni(dppp) complexes with fullerenes C_{60} (**1**) (*a*)[21] and C_{70} (**4**) (*b*);[22] the structure of Co(dppf)(PhCN)(η^2-C_{60}) (**6**) (*c*).[26]

Table 1. Geometric parameters of the NiL(η^2-C_{60}) complexes (L = dppe, dppp and dppf).[23]

Parameter	Ni(dppe)(η^2-C_{60})		Ni(dppp)(η^2-C_{60})	Ni(dppf)(η^2-C_{60})
Conformation of the Ni(L) moiety	Planar	Twisted	Planar	Planar
Average Ni – C(C_{60}) bond length /Å	1.936(6)	1.952(2)	1.950(2)	1.977(3)
Average Ni – P(L) bond length /Å	2.142(2)	2.144(2)	2.1550(5)	2.198(1)
Coordinated 6 : 6-bond length in C_{60} /Å	1.475(8)	1.485(9)	1.488(3)	1.490(4)
Average 6 : 6-bond length in C_{60} /Å	1.381(9)	1.386(12)	1.388(3)	1.389(4)
P – Ni – P angle /deg	89.24(7)	89.13(8)	100.67(2)	106.33(3)

sensitive to the action of oxygen, especially in solution. For example, the spectrum of a Ni(dppp)(η^2-C_{70}) solution exposed to air rapidly changes: in a few minutes, the spectrum shows only the absorption bands of pure C_{70}. This attests to decomposition of the complex under the action of oxygen.

Thus, the nickel complexes with fullerenes contain a neutral fullerene and nickel in the zero oxidation state with diamagnetic electronic configuration d^{10}. They strongly resemble the previously studied palladium and platinum complexes.[42, 45, 46]

III.2. Cobalt complexes with fullerene C_{60}

To synthesize cobalt complexes with fullerene, the presence of an additional ligand is necessary; the latter is coordinated to the cobalt atom and increases its coordination number. In the absence of such ligands, no cobalt complexes with fullerene are formed. In some cases, if this is allowed by the diphosphine ligand size, the cobalt atom, increasing its C.N., can coordinate simultaneously to two fullerene molecules, which leads to coordination dimers like in Co(dppe) complexes.

Cobalt complexes form by the same scheme as the nickel compounds; however, the introduction of ligands L′ is necessary [reaction (6)].

$$Co(L)Br_2 + C_{60} + 2\,Red + L' \longrightarrow Co(L)(L')(\eta^2\text{-}C_{60}) \qquad (6)$$

Red is zinc + fluorenone ketyl; L = Ph_3P, dppf, dppe;
L′ = PhCN

We have synthesized for the first time fullerene C_{60} complexes with cobalt in the zero oxidation state. The complexes form upon the reduction of a C_{60} + Co(L)Cl_2(Br_2) mixture only in the presence of benzonitrile, which is coordinated to cobalt together with fullerene and diphosphine to give CoL(PhCN)(η^2-C_{60}) [L = dppe (**5**), dppf (**6**)],[26] where cobalt has a distorted square-pyramidal environment (see Fig. 5 *c*). Cobalt is coordinated to a 6 : 6 bond of C_{60} in an η^2 fashion, and the Co – C bond length is 2.008(3) – 2.060(3) Å. It has been demonstrated that the increase in the P – Co – P angle from 88.51(2)° in Co(dppe) to 104.94(2)° in Co(dppf), as in the case of nickel, leads to the elongation of the Co – C(C_{60}) and Co – P bonds by 0.04 – 0.06 Å.

The Co^0 atom is paramagnetic since it has the d^9 electronic configuration and spin $S = 1/2$. The presence of the spin on the cobalt atom is supported by the fact that the EPR spectra of compounds **5** and **6** show strong asymmetric signals with g values 2.03 – 2.21 (for complex **5**) and 2.10 – 2.27 (for **6**), characteristic of Co^0. Effective magnetic moments (1.86 and 1.83 μ_B for complexes **5** and **6**, respectively) also point to the low-spin state $S = 1/2$ for Co^0. At the same time, the absence of absorption bands of C_{60}^- in the near-IR range and of the signals of $C_{60}^{-\bullet}$ in the EPR spectra is unambiguous evidence that fullerenes in these complexes are neutral. Thus, there is no noticeable charge transfer from CoL(PhCN) to C_{60} in these compounds. The large distance between the cobalt atoms of CoL(PhCN)(η^2-C_{60}) packed in crystals of compounds **5** and **6** is responsible for their pure paramagnetic behaviour, without noticeable magnetic coupling of spins. The EPR signals due to Co^0 in compounds **5** and **6** exposed to air gradually disappear. This can be caused by the conversion of paramagnetic cobalt(0) to diamagnetic cobalt(I) under the action of air oxygen. It is possible that, as in the case of nickel complexes, the oxidation leads to decomposition of the complex.

III.3. Coordination dimers of fullerene C_{60} with nickel and cobalt

Reduction of a mixture of (Ph_3P)$Ni^{II}Cl(\eta^5$-Cp) and C_{60} by two equivalents of a reducing agent at 160 °C in *o*-dichlorobenzene leads to elimination of the cyclopentadienyl ligand. The presence of only one Ph_3P ligand at the nickel atom makes it coordinatively unsaturated so that it can coordinate simultaneously to two fullerene molecules to form the coordination dimer {Ni(Ph_3P)}$_2$(μ-η^2,η^2-C_{60})$_2$ (**7**) (Fig. 6 *a*).[24] Each nickel atom links two fullerene molecules in an η^2 fashion; the Ni – C bond length is 2.001(3) – 2.037(3) Å (see Fig. 6 *a*). The nickel atoms are coordinated to two 6 : 6 bonds of the same hexagon of C_{60}, and these bonds are elongated to 1.447(3) – 1.449(3) Å as compared with the 6 : 6 bonds of C_{60} not involved in coordination [1.390(4) Å]. The nickel atom is also coordinated to one triphenylphosphine ligand; thus, the nickel environment contains four carbon atoms and one phosphorus atom. The Ni···Ni distance in the dimer is 3.442(3) Å. The fullerene cages are closely spaced: the distance between the fullerene centres is only 9.716 Å. As a result, a very short C···C contact 2.679(4) Å] appears between the fullerene cages; this contact essentially exceeds the C – C bond length in fullerene dimers (C_{60}^-)$_2$ [1.587(4) – 1.597(4) Å];[40, 79 – 84] therefore, no fullerene dimerization is observed. According to the EPR and near-IR spectra, fullerenes in complex **7** are neutral; therefore, nickel should have the diamagnetic electronic configuration d^{10}. Density functional theory (DFT) calculations for compound **7** have shown that the highest occupied molecular orbital (HOMO) in the dimer is localized at the nickel atoms, while the higher-lying LUMOs (LUMO and LUMO + 1) are mainly localized on C_{60}. As a result, the dimer has a singlet diamagnetic state with the gap between the HOMO and LUMO exceeding 1.64 eV.

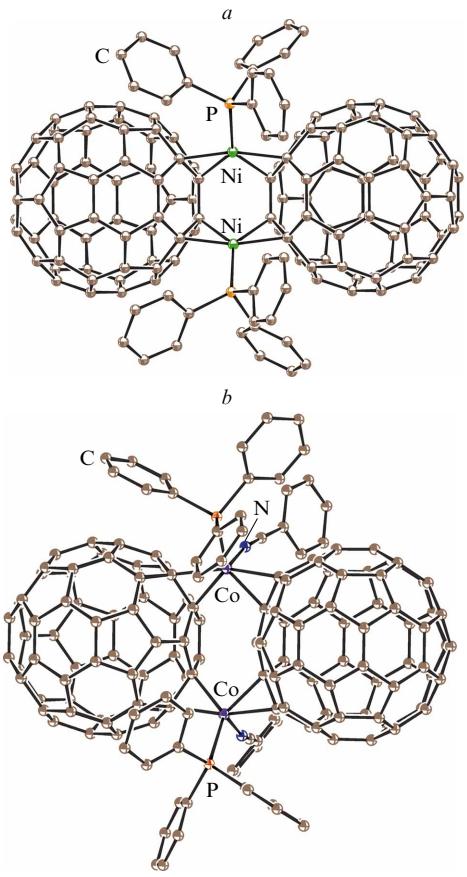


Figure 6. Molecular structures of coordination dimers $\{Ni(Ph_3P)\}_2(\mu\text{-}\eta^2,\eta^2\text{-}C_{60})_2$ (**7**) (*a*)[24] and $\{Co(Ph_3P)(PhCN)\}_2(\mu\text{-}\eta^2,\eta^2\text{-}C_{60})_2$ (**8**) (*b*).[27]

In the coordination dimer $\{Co(Ph_3P)(PhCN)\}_2(\mu\text{-}\eta^2,\eta^2\text{-}C_{60})_2$ (**8**) with zero-oxidation-state cobalt (see Fig. 6 *b*),[27] two cobalt atoms link two fullerene molecules in an η^2 fashion through the Co–C bonds 2.048(3)–2.128(2) Å in length. The 6:6 bonds of C_{60} involved in coordination are elongated from the average value of 1.392(3) to 1.464(3) Å. The cobalt atom is additionally coordinated to one triphenylphosphine ligand and one benzonitrile molecule. As a result, the cobalt atom is at the centre of a pentagonal pyramid with the base formed by four carbon atoms of C_{60} and one phosphorus atom of Ph_3P and one nitrogen atom of PhCN at the top of the pyramid. Like in the Ni dimer, the fullerene cages in the molecule of **8** are closely spaced, with the distance between the centres being 9.696 Å. However, in the cobalt dimer, the molecules are arranged with respect to each other in such a way that the van der Waals C···C contacts between the fullerenes [2.815(2) Å] are noticeably longer than in the nickel dimer. Two cobalt atoms are coordinated to 6:6 bonds from two hexagons of C_{60} separated by one pentagon. This leads to an increase in the distance between the metal atoms, as compared with the nickel dimer, to 5.308(3) Å. According to EPR and near-IR spectra, the fullerenes in complex **8** are neutral, like in the monomeric compounds described in the previous section. In this case, the cobalt atoms should have zero oxidation state and paramagnetic electronic configuration d^9. There is no direct overlap of orbitals between the cobalt atoms. It is likely that the major mechanism of magnetic coupling of the cobalt atoms in dimer **8** is polarization of the π-electron cloud of the fullerene molecules.

According to magnetic measurements, the cobalt atoms have spin $S = 1/2$ and an isotropic signal in EPR spectra with the *g* value 2.3053 at 298 K. At room temperature, the effective magnetic moment of the molecule of **8** is 2.76 μ_B, which points to the triplet state of the dimer (the theoretical value for the triplet with $S = 1$ is 2.83 μ_B). Although the EPR spectrum of complex **8** does not show a pure triplet signal, there are signs of the triplet state: these are a signal at half the magnetic field of the basic signal characteristic of triplets and weak signals with triplet splitting. The Weiss temperature, estimated in the range 60–300 K, is −34 K, which points to strong antiferromagnetic spin coupling. At temperature < 60 K, the dimer transforms to the diamagnetic singlet ground state ($S = 0$), which leads to a decrease in the magnetic susceptibility of a sample and to a sharp decrease in the EPR signal intensity. The temperature dependence of molar magnetic susceptibility is described well by the Heisenberg model for an isolated pair of antiferromagnetically coupled spins with the exchange coupling parameter $J/k_B = -28.6$ K, which points to rather strong magnetic interactions between the spins localized on the cobalt atoms. DFT calculations have shown that the SOMO (singly occupied molecular orbital) of the dimer is made up of the d_{z^2} orbital of the cobalt atom and the π orbital of benzonitrile, so that the unpaired electron is localized on the Co(PhCN) moiety. The singlet state is the ground state and is very close in energy to the excited triplet state, which is consistent well with experimental data.[27]

Thus, coordination compounds of this type can be promising in design of magnetic systems since fullerenes, even in the neutral state, are able to rather efficiently transfer magnetic interactions between coordinated paramagnetic metal atoms.

III.4. Fullerene dimerization through coordination of bridging metal atoms

In dimers and polymers where the fullerene anions are linked through carbon–carbon bonds, the shortened distances between the fullerenes and a significant overlap of orbitals are observed, which enhances magnetic interactions between the fullerene anions. For example, the dimer $(C_{60}^-)_2$ formed through two C–C bonds and having spin $S = 1/2$ on each C_{60}^- anion is characterized by very strong antiferromagnetic spin coupling ($J/k_B = -44.7$ K).[39] Polymers can exhibit metallic conductivity, and conducting electrons can move directly along the polymeric fullerene chains.[10–12] Therefore, it is an extremely interesting task to synthesize dimers and, possibly, polymers in which fullerenes are linked not only by bridging metal atoms but also by C–C bonds.

The above structures demonstrate that, upon coordination to bridging metal atoms, the fullerene molecules come closer together, but this does not lead to the formation of the C–C bond between them. It turns out that some ligands (for example, dppe) allow the fullerenes in coordination dimers to come so close to each other that, if their cages are favourably oriented, two fullerene π bonds are broken and two new σ bonds form between the cages. This gives a new type of dimer $\{Co(dppe)\}_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}\eta^2\text{:}\eta^2\text{-}[(C_{60})_2]\}$ (**9**) in which the fullerene cages are linked by two bridging cobalt atoms and two C–C bonds (Fig. 7).[28]

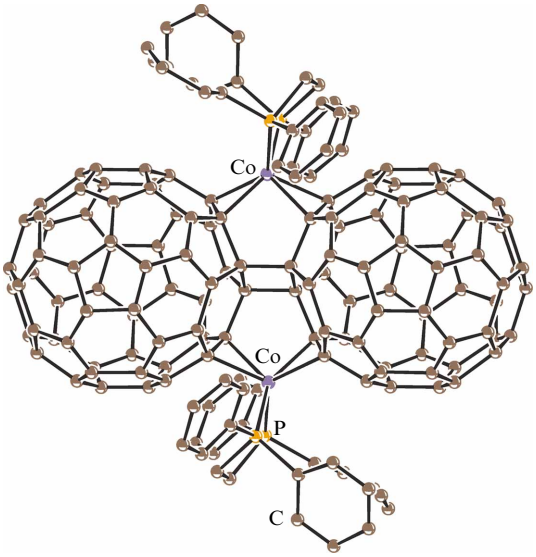


Figure 7. Molecular structure of coordination dimer $\{Co(dppe)\}_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}\eta^2\text{:}\eta^2\text{-}[(C_{60})_2]\}$ (**9**).[28]

Two cobalt atoms are η^2-coordinated to 6 : 6 bonds of two neighbouring C_{60} molecules; the Co – C bond lengths are within 2.080(3) – 2.096(4) Å. Each cobalt atom is additionally coordinated to the diphosphine ligand, which leads to a distorted octahedral environment composed of four carbon atoms of C_{60} and two phosphorus atoms. Coordination to two bridging cobalt atoms brings the fullerene molecules closer together so that they can dimerize through two intercage C – C bonds with a length of 1.571(4) Å (see Fig. 7). The distance between the C_{60} centres in such a dimer is 9.07 Å. It is worth noting that the intercage bond lengths and the distances between the fullerene centres in compound **9** are close to those in the neutral dimer $(C_{60})_2$ [9.05 and 1.575(7) Å], respectively[85] and the negatively charged dimer $(C_{60}^{-})_2$ [9.07 and 1.581(3) Å, respectively],[37,39] in which the fullerenes are also linked by two C – C bonds. It is evident that the dimerization is caused by the fact that the coordination of bridging metal atoms not only brings the fullerene molecules closer together but also orients them so that two 6 : 6 π bonds of C_{60} are arranged exactly opposite each other, which facilitates dimerization. The fullerene molecules in dimers **7** and **8** are oriented in a different way: here, less active 6 : 5 bonds are arranged opposite each other, and these bonds are fixed so that the distance between the carbon atoms is too long for dimerization (2.67 – 2.81 Å).[23,27]

The cobalt atoms in dimer **9** are at a distance of 6.450(5) Å from each other, which is noticeably longer than the Co···Co distance in dimer **8** [5.308(3) Å].[27] The dimers are packed in crystal in such a way that fullerene cages form zigzag chains with intercentre distances of 9.85 and 9.88 Å. These distances are noticeably smaller than the van der Waals diameter of C_{60} (10.18 Å); therefore, there are a large number of van der Waals C···C contacts between the dimers with distances within 3.01 – 3.41 Å.

Near-IR spectra demonstrate that, like in other cobalt complexes, fullerenes in complex **9** remain neutral while the cobalt atom has electronic configuration d^9. Magnetic susceptibility for this compound has not been directly measured; however, DFT calculations predict that dimer **9**, like dimer **8**, has a singlet ground state and a closely spaced excited triplet state, the gap between them being roughly the same as in dimer **8**. The d orbital of cobalt and the π orbital of the $(C_{60})_2$ dimer make the major contribution to the SOMO of the dimeric complex so that this molecular orbital is localized not only on the cobalt atom but also partially on fullerene. Spin density is localized mainly on the cobalt atoms. Due to polarization of the π-electron system, the $(C_{60})_2$ dimer as well as the C_{60} molecule can efficiently transfer magnetic interactions between the spins localized on two cobalt atoms.

It should be noted that we were the first to synthesize dimeric fullerene structure of this type. Analysis of the fullerene structures with bridging metal atoms shows that the arrangement of metal atoms on the fullerene surface and, hence, the geometry of these compounds essentially depends on the number and size of additional ligands (Ph_3P, PhCN, dppe). Thus, by varying the ligands, one can modify the structure and, hence, the properties of similar dimers. We believe that coordination of two Co(dppe) groups to one fullerene molecule will also lead to a decrease in the distance between the fullerene centres and, hence, will promote fullerene polymerization.

III.5. Coordination polymers of fullerene C_{60}

The coordination polymer (**10**) of fullerene C_{60} with nickel atoms additionally coordinated to trimethylphosphine ligands has been synthesized (Fig. 8).[25] For this purpose, a mixture of $Ni^{II}(Me_3P)_2Cl_2$ and C_{60} was reduced with zinc in *o*-dichlorobenzene in the presence of coordinating solvents (DMF or PhCN). The presence of coordinating solvents is essential for crystal growth since in neat *o*-dichlorobenzene

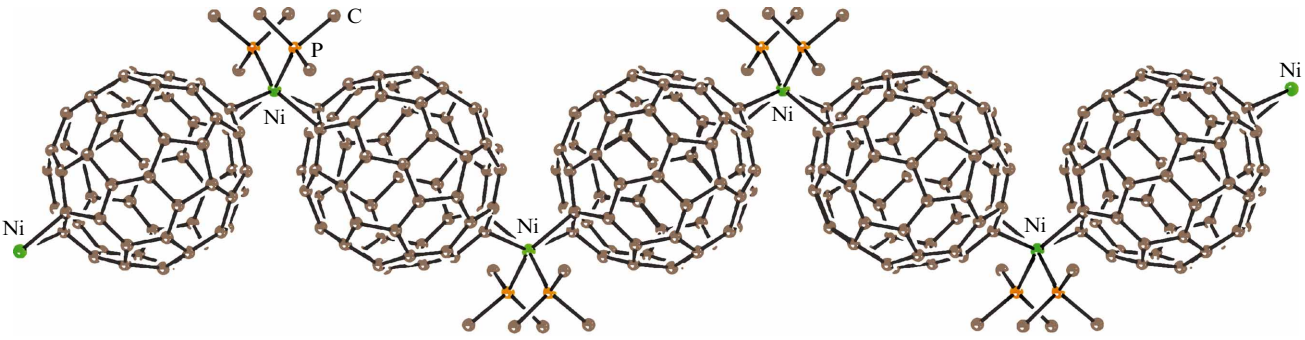


Figure 8. Structure of the coordination polymer of fullerene C_{60} with nickel $[\{Ni(Me_3P)_2\}(\mu\text{-}\eta^2,\eta^2\text{-}C_{60})]_\infty$ (**10**).[25]

the polymer is quantitatively precipitated as a powder within one day. When strongly coordinating solvents, for example, pyridine, are used as additives, the complexation with fullerene can be completely suppressed. This was the first coordination polymer with fullerenes obtained in the form of crystals. The previously known polymers of C_{60} with platinum, palladium and europium were prepared as amorphous powders, and their structure is unknown.[86–89] In polymer **10**, each nickel atom is η^2-coordinated to 6 : 6 bonds of two fullerene cages; the Ni – C(C_{60}) bond lengths are within 2.087(8) – 2.149(8) Å. In addition, the nickel atom is coordinated to two trimethylphosphine ligands to form a distorted octahedral environment (see Fig. 8). In polymer **10**, like in coordination dimers, the fullerene cages come closer together (the distance between the C_{60} centres is 9.693 Å), and there are two short C···C contacts between them [2.923(7) Å]. Small additional ligands at the nickel atom enable close packing of polymer chains in crystal: the distance between the centres of C_{60} from neighbouring chains is 9.92 Å, and there are numerous van der Waals contacts between the fullerenes of neighbouring chains. As a result, the crystal structure of **10** is a three-dimensional close packing of coordination polymer chains.

According to near-IR and EPR spectra, the fullerenes in the polymer are in the neutral state; therefore, the nickel atom is in the zero oxidation state and has a diamagnetic configuration d^{10}. DFT calculations confirm the diamagnetic state of the polymer with the singlet – triplet splitting > 1.37 eV.

Thus, the proposed approach opens the way to coordination polymers of fullerenes; they can be synthesized as crystals, which makes it possible to study in detail their structure and properties. Of special interest is the possibility of increasing the number of metal-containing groups $\{Ni(Me_3P)_2\}$ coordinated to the fullerene cage. This can lead to coordination polymers of more complicated structure, including two-dimensional polymers.

III.6. Complexes with fullerene anions

To synthesize complexes with fullerene anions, fullerene and sometimes the metal-containing moiety should be reduced in the course of complexation.

Previously, the reaction of sodium or bis(trimethylphosphoranylidene)ammonium (PPN^+) metal carbonylates with neutral fullerenes has afforded a series of anionic complexes of C_{60}, C_{70} and some other higher fullerenes: $PPN^+\{Co(CO)_3(\eta^2\text{-}C_{60})\}^-$, $PPN^+\{M(CO)_4(\eta^2\text{-}C_{60})\}^-$ (M = Mn, Re), $PPN^+\{(\eta^5\text{-}Cp)M(CO)_2(\eta^2\text{-}C_{60})\}^-$ (M = Mo, W).[90–94] These compounds have been synthesized as powders;[90–93] crystals have been prepared only for $PPN^+\{Mn(CO)_4(\eta^2\text{-}C_{60})\}^-$, which has been structurally characterized.[94] In the near-IR spectra of these complexes, absorption bands of the C_{60}^- anion are not observed. Hence, fullerenes are in the neutral state, and the negative charge is localized on the metal-containing moiety to give the $\{Mn(CO)_4\}^-$ or $\{(\eta^5\text{-}Cp)Mo(CO)_2\}^-$ anions.

We have developed a new method of synthesis of anionic complexes from fullerene radical anion salts and corresponding neutral coordination compounds.[29] The reaction of $PPN^+(C_{60}^{-\bullet})$ or $PPN^+(C_{70}^{-\bullet})$ with cyclopentadienyl(tricarbonyl)molybdenum $\{(\eta^5\text{-}Cp)Mo(CO)_3\}_2$ and subsequent slow precipitation with hexane yielded crystals of $PPN^+\{(\eta^5\text{-}Cp)Mo(CO)_2(\eta^2\text{-}C_{60})\}^-$ (**11**) and $PPN^+\{(\eta^5\text{-}Cp)Mo(CO)_2(\eta^2\text{-}C_{70})\}^-$ (**12**). In complexes **11** and **12**, the molybdenum atom is coordinated to a 6 : 6 bond of C_{60} or a bond at the junction of two hexagons of C_{70} (this band is of the *a* – *b* type). The Mo – C(fullerene) bond lengths are within 2.246(2) – 2.252(6) Å. The UV/Vis and near-IR spectrum of compound **11** is shown in Fig. 9 *a*. The visible region of the spectrum shows strong bands at 452 and 715 nm. These bands are assigned to charge transfer from the metal to fullerene; they are observed in the spectra of nearly all fullerene complexes.[2,3,21–30] Although the spectrum of complex **11** shows the absorption band due to the C_{60}^- anion at 1064 nm (see Fig. 9 *a*, shown by the arrow), its intensity is small; *i.e.*, the C_{60}^- anions in this compound are present only as an impurity. It is known that the IR spectrum of neutral fullerene C_{60} shows an absorption band at 1429 cm^{-1} assigned to the $F_{1u}(4)$ mode. This band is sensitive to charge transfer to the fullerene molecule and is shifted to 1388 – 1396 cm^{-1} in the spectra of radical anion C_{60} salts.[20] In the spectra of neutral complexes, the position of this band usually varies within 1412 – 1420 cm^{-1} (Refs 21, 23 – 30). In the spectrum of compound **11**, the $F_{1u}(4)$ mode is observed at 1416 cm^{-1}, which corresponds to the formation of a neutral complex. Compound **11** is diamagnetic, and the contribution of paramagnetic impurities does not exceed 2% of the total C_{60} content. Thus, although compound **11** is an anionic complex, it contains neutral fullerene C_{60}. This is explained by charge transfer from the $C_{60}^{-\bullet}$ radical anion to $(\eta^5\text{-}Cp)Mo^I(CO)_2$ and formation of neutral diamagnetic intermediates C_{60}^0 and $(\eta^5\text{-}Cp)Mo^0(CO)_2^-$, which form the coordination anion $\{(\eta^5\text{-}Cp)Mo(CO)_2(\eta^2\text{-}C_{60})\}^-$. Analogously, the $\{(\eta^5\text{-}Cp)Mo(CO)_2(\eta^2\text{-}C_{70})\}^-$ coordination anion in compound **12** is formed from C_{70}^0 and $\{(\eta^5\text{-}Cp)Mo^0(CO)_2\}^-$ (Ref. 29).

To prevent charge transfer from the fullerene anion to the coordinating metal-containing moiety, the latter should have strong donor properties. Coordination of the pentamethylcyclopentadienyl ligand significantly enhances the donor properties of the metal atom. In particular, metals with two Cp* ligands are among the strongest organometallic reducing agents. The first oxidation potentials of Cp_2^*Co and Cp_2^*Cr are −1.55 and −1.04 V, respectively.[95] On average, the oxidation potentials of transition-metal complexes containing two Cp* ligands are shifted by 0.5 V toward negative values as compared with analogous cyclopentadienyl complexes.[95]

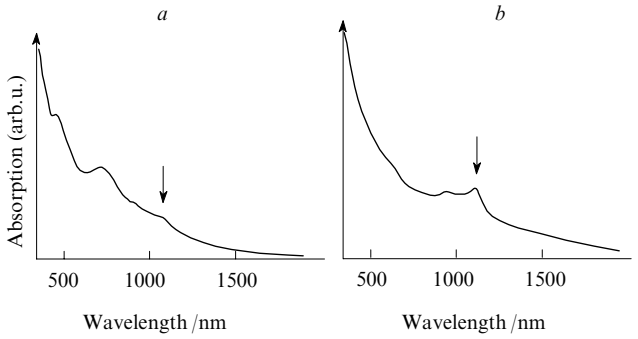


Figure 9. UV/Vis and near-IR spectra of $PPN^+\{(\eta^5\text{-}Cp)Mo^I(CO)_2(\eta^2\text{-}C_{60})\}^-$ (**11**) (*a*) and $PPN^+\{(\eta^5\text{-}Cp^*)Mo^I(CO)_2(\eta^2\text{-}C_{60})\}^-$ (**13**) (*b*).[29]
The spectra were recorded as KBr pellets prepared under anaerobic conditions.

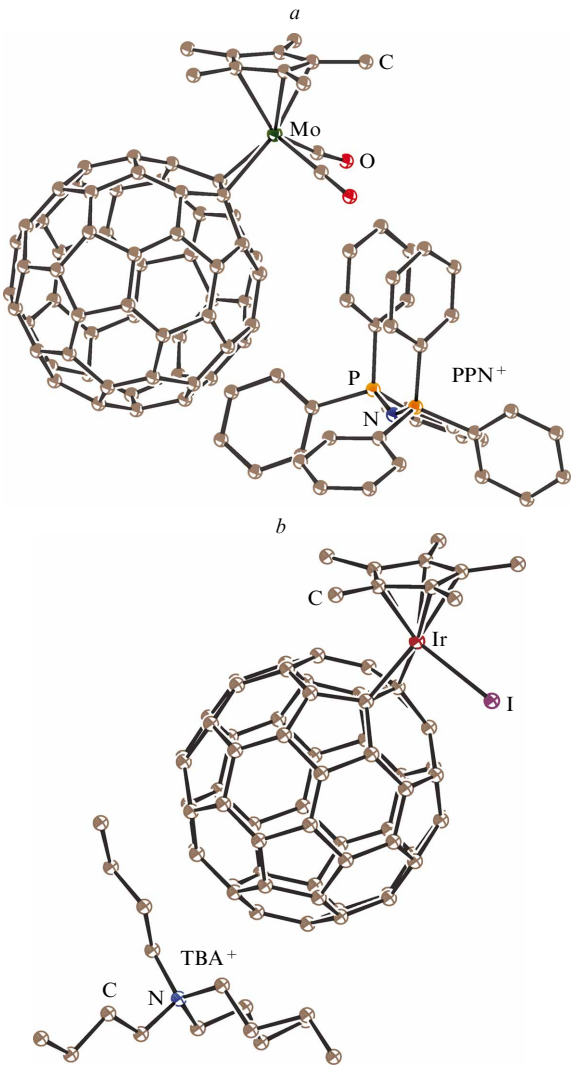


Figure 10. Molecular structures of anionic complexes of fullerene C_{60}: $PPN^+\{(\eta^5\text{-Cp*})Mo^I(CO)_2(\eta^2\text{-}C_{60})\}^-$ (**13**) (*a*)[29] and $TBA^+\{(\eta^5\text{-Cp*})Ir^{II}I(\eta^2\text{-}C_{60})\}^-$ (**15**) (*b*).[30]

The cyclopentadienyl ligand in compound **11** was replaced by the pentamethylcyclopentadienyl ligand through the reaction of $PPN^+(C_{60}^{-\bullet})$ with $\{(\eta^5\text{-Cp*})Mo^I(CO)_2\}_2$. Slow precipitation with hexane afforded crystals of $PPN^+\{(\eta^5\text{-Cp*})Mo^I(CO)_2(\eta^2\text{-}C_{60})\}^-$ (**13**).[29] In this compound, the molybdenum atom is coordinated to a 6:6 bond of C_{60} [the Mo–C(C_{60}) bond length is 2.287(6) Å] (Fig. 10 *a*). Spectral properties of compound **13** differ considerably from those of complexes **11** and **12**. Compound **13** (violet in solution and in the solid state) have no strong absorption bands in the visible range (see Fig. 9 *b*) observed for compound **11** (see Fig. 9 *a*). Rather strong absorption bands appear in the near-IR range at 936 and 1088 nm (see Fig. 9 *b*), characteristic of the C_{60}^- anions.[20] The $F_{1u}(4)$ mode of C_{60} in the IR spectrum of compound **13** is shifted to 1392 cm^{-1}, which is typical of C_{60} radical anion salts.[20, 77]

DFT calculations of the complex anions in compounds **11** and **13** support the conclusions drawn from optical spectra. Fullerene in complex **13** has a noticeably larger negative charge than in complex **11**. This is explained by stronger charge transfer from the metal atom d orbital to the antibonding π* orbital of fullerene because of the stronger donor properties of the Cp* ligand as compared with Cp. Thus, the negative charge in the $\{(\eta^5\text{-Cp*})Mo^I(CO)_2(\eta^2\text{-}C_{60})\}^-$ anion is essentially localized on fullerene rather than on the metal-containing moiety as in compounds **11** and **12**. However, despite the fact that fullerene in complex **13** exists in the anionic form, the EPR spectra and measurements with a superconducting quantum interference device (SQUID magnetometry) demonstrate that the compound is diamagnetic like complexes **11** and **12**.

A method of double reduction has also been used, which allows one not only to synthesize complexes with fullerene anions but also to reduce the metal-containing moiety. For example, the reduction of a mixture of fullerene C_{60} and vanadyl phthalocyanine [$V^{IV}OPc(2-)$] in solution by sodium fluorenone ketyl (fluorenone) in the presence of TBA^+Br^- (TBA is tetra-n-butylammonium) gives two salts at a time: $TBA^+(C_{60}^{-\bullet})$ and $TBA^+\{V^{IV}OPc(3-)\}^{-\bullet}$ [reaction (7)]. The $\{V^{IV}OPc(3-)\}^{-\bullet}$ radical anion exhibits strong donor properties and reduce compounds with reduction potentials to −0.8 V, converting to the neutral state.[96] Neutral $V^{IV}OPc(2-)$ is insoluble in common solvents and quantitatively precipitates from solution. The reaction of a mixture of two salts with the $\{(\eta^5\text{-Cp*})Ir^{III}Cl_2\}_2$ dimer leads to the reduction of Ir^{III} to Ir^{II} and quantitative precipitation of neutral $V^{IV}OPc(2-)$ [reaction (8)]. The resulting complex $(\eta^5\text{-Cp*})Ir^{II}Cl$ reacts with the radical anion salt $TBA^+(C_{60}^{-\bullet})$ rather than with neutral fullerene to give the anionic complex $TBA^+\{(\eta^5\text{-Cp*})Ir^{II}Cl(\eta^2\text{-}C_{60})\}^-$ (**14**). The use of $\{(\eta^5\text{-Cp*})Ir^{III}I_2\}_2$ as an reactant leads to $TBA^+\{(\eta^5\text{-Cp*})Ir^{II}I(\eta^2\text{-}C_{60})\}^-$ (**15**)[30] (see Fig. 10 *b*) in which the chlorine atom at iridium is replaced by an iodine atom.

$$C_{60} + V^{IV}OPc(2-) + 2\,TBA^+Br^- + \quad (7)$$
$$+ 2\,Na^+\{(fluorenone)^{-\bullet}\} \longrightarrow TBA^+(C_{60}^{-\bullet}) +$$
$$+ TBA^+\{V^{IV}OPc(3-)^{-\bullet}\} + 2\,NaBr + 2\,fluorenone$$
$$TBA^+(C_{60}^{-\bullet}) + TBA^+\{V^{IV}OPc(3-)^{-\bullet}\} + \quad (8)$$
$$+ 0.5\,\{(\eta^5\text{-Cp*})Ir^{III}Cl_2\}_2 \longrightarrow TBA^+\{(\eta^5\text{-Cp*})Ir^{II}Cl(\eta^2\text{-}C_{60})\}^- +$$
14
$$+ TBA^+Cl^- + V^{IV}OPc(2-)\downarrow$$

Iridium is coordinated to a 6:6 bond of C_{60} [the Ir–C(C_{60}) bond length is within 2.123(10)–2.131(9) Å], and the coordination is accompanied by a considerable elongation of the C–C bonds at the 6:6 ring junctions from the average values 1.382(16)–1.389(16) Å to 1.521(14)–1.532(13) Å. Both compounds are violet in solution and in the solid state, which is typical of C_{60} radical anion salts. Like the spectrum of compound **13**, the spectra of complexes **14** and **15** show no strong absorption bands in the visible range that could be attributed to metal–fullerene charge transfer (Fig. 11). The near-IR range shows only absorption bands at 940 and 1040 (for complex **14**) and 926 and 990 nm (for complex **15**) assigned to the C_{60}^- anion.[20, 77] The IR spectra of compounds **14** and **15** show a new absorption band at 1398 cm^{-1} arising from the C_{60}^- anion. As can be seen, C_{60}^- is unable to reduce $(\eta^5\text{-Cp*})Ir^{II}$ to $(\eta^5\text{-Cp*})Ir^I$ and retains its anionic state. Thus, the negative charge in the $\{(\eta^5\text{-Cp*})Ir^{II}Cl(\eta^2\text{-}C_{60}^-)\}$ and $\{(\eta^5\text{-Cp*})Ir^{II}I(\eta^2\text{-}C_{60}^-)\}$ anions is mainly localized on fullerene.

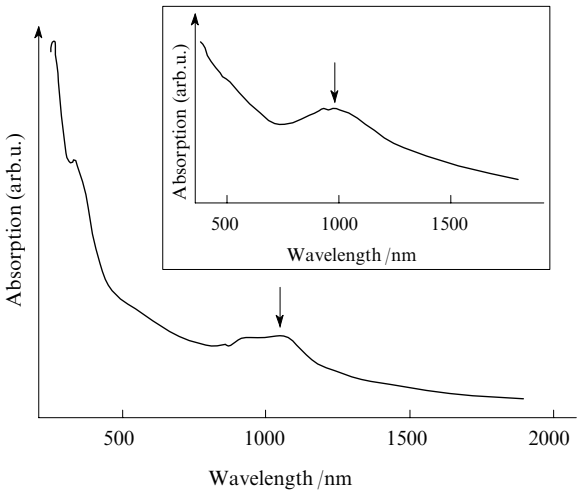


Figure 11. UV/Vis and near-IR spectrum of $TBA^+\{(\eta^5\text{-Cp*}).Ir^{II}Cl(\eta^2\text{-}C_{60})\}^-$ (**14**).[30]
Inset: the near-IR spectrum of $TBA^+\{(\eta^5\text{-Cp*})Ir^{II}I(\eta^2\text{-}C_{60})\}^-$ (**15**). The spectra were recorded for KBr pellets prepared under anaerobic conditions.

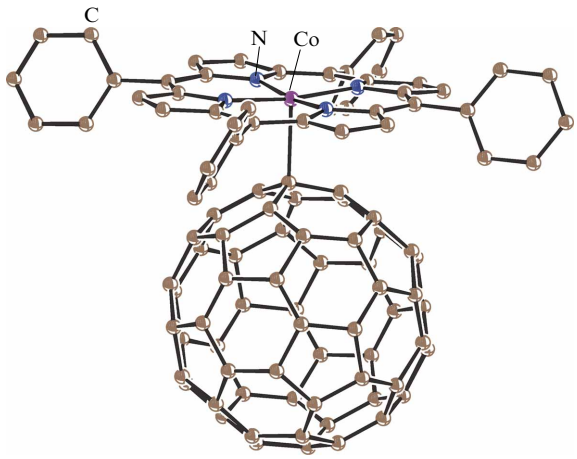


Figure 12. Molecular structure of the complex anion $\{Co^{II}(TPP)(C_{60}^-)\}$ in $\{cryptand[2,2,2](Na^+)\}\{Co^{II}(TPP)(C_{60}^-)\}\cdot 2\,C_6H_4Cl_2$.[97]
The Co–C(C_{60}) bond length is 2.262(2) Å.

Magnetic measurements for complexes **14** and **15** demonstrate the diamagnetism of both compounds. Initial $(\eta^5\text{-Cp*})Ir^{II}I$ and $C_{60}^{-\bullet}$ species forming complex **15** are paramagnetic and should have spin $S = 1/2$. However, DFT calculations predict that the formation of the coordination bond between Ir^{II} and $C_{60}^{-\bullet}$ in compound **15** leads to spin pairing so that compound **15** has a diamagnetic singlet ground state (with a singlet–triplet splitting of >0.8 eV). At the same time, calculations show that the charges in complex **15** are distributed in such a way that fullerene C_{60} has a considerable negative charge, while the oxidation state of iridium is close to $+2$. Spin pairing caused by formation of coordination or covalent bonds between two paramagnetic species is well known. This occurs, for example, when paramagnetic radical anions $C_{60}^{-\bullet}$ dimerize to form diamagnetic dimers $(C_{60}^-)_2$ linked through a C–C single bond.[79–84]

Yet another example is spin pairing upon the formation of a σ bond between cobalt(II) tetraphenylporphyrin (TPP) or octaethylporphyrin (OEP) and radical anions of fullerene $C_{60}^{-\bullet}$ or dicyanofullerene $C_{60}(CN)_2^{-\bullet}$ (Refs 82, 97–102). Formally, these compounds should contain two paramagnetic species — Co^{II}(porphyrin) and $C_{60}^{-\bullet}$. However, magnetic measurements demonstrate that the $\{Co^{II}(TPP)(C_{60}^-)\}$ (Fig. 12), $\{Co^{II}(TPP)[C_{60}(CN)_2^-]\}$ and $\{Co^{II}(OEP)(C_{60}^-)\}$ coordination anions are diamagnetic.[97–100] It should be noted that, in this case, diamagnetism is not associated with charge transfer from the fullerene anion to cobalt(II) porphyrin since (according to optical spectra) fullerenes retain their anionic state. In some cases, dissociation of coordination bonds is observed, which leads to the appearance of the contribution of spins $S = 1/2$ localized on both the Co^{II} atoms and the $C_{60}^{-\bullet}$ radical anions;[97,100] the compounds are converted from the diamagnetic to paramagnetic state. Compounds of this type have been covered in reviews.[82,102]

The direct formation of coordination bonds between two paramagnetic species leads, as a rule, to diamagnetic products in which the anionic state of fullerenes can persist. However, to achieve high conductivity and promising magnetic properties, a complex should have spins and be paramagnetic. For synthesis of such compounds, one of the coordinating species should be diamagnetic. Indeed, the complexes of paramagnetic cobalt in the zero oxidation state with neutral fullerenes have spin state $S = 1/2$.[26,27] Spin can also be retained upon coordination of the fullerene radical anion to diamagnetic metal atoms. Spatial separation of paramagnetic species even by one diamagnetic atom can prevent spin pairing so that the spins are retained. For example, tin phthalocyanine radical anion $(Sn^{II}Pc(3-)\}^{-\bullet}$ gives a complex with a paramagnetic transition metal (Mo^I) through the formation of an Sn–Mo bond. The two paramagnetic species in $\{cryptand[2,2,2](Na^+)\}\{(\eta^5\text{-Cp})Mo^I.(CO)_2[(Sn^{II}Pc(2-)(Sn^{II}Pc(3-)^{-\bullet}]\}$ are separated only by a diamagnetic tin(II) atom. This makes it possible to retain the spins on both the phthalocyanine radical anion $\{Pc(3-)^{-\bullet}\}$ and the Mo^I atoms; there is strong magnetic exchange coupling between these spins.[103] Unfortunately, this variant is hard to be realized for fullerene complexes.

IV. Conclusions

Fullerene complexes attract special attention of researchers since, owing to their optical and magnetic properties, they are candidates for use in modern technologies. Transition-metal (nickel, cobalt) complexes of fullerenes can be synthesized through the reduction of divalent metal salts containing additional phosphine or diphosphine ligands in the presence of fullerenes. This leads to monomeric complexes. When the metal atoms serve as bridges between the fullerenes, coordination dimers are formed. It should be emphasized that upon coordination of fullerenes to bridging metal atoms, fullerenes are able to dimerize or, probably, polymerize through the formation of new C–C bonds between the fullerenes. Such dimers and polymers, especially if metal–fullerene charge transfer is realized, can exhibit promising magnetic and conducting properties.

Complexes with anionic fullerenes can be synthesized either by the reaction of a transition metal (molybdenum, iridium) with a fullerene radical anion salt or by the simultaneous reduction of both the fullerene and the

metal-containing species. Of crucial importance is the electron density distribution over the fragments in the course of formation of the coordination bond, which is responsible for diamagnetism or paramagnetism of the produced compounds and, hence, has an essential effect of their properties. In a coordination compound, the anionic state of fullerene is retained if the fullerene is unable to reduce the metal-containing moiety. This is the case when the transition-metal atom is bonded to a ligand with strong donor properties (for example, the pentamethylcyclopentadienyl ligand). However, if there are spins on the fullerene radical anion and coordinating metal atom, the formation of the coordination bond between them leads, as a rule, to spin pairing to give a diamagnetic complex. If one of the components is diamagnetic, the second component can retain its spin so that the resulting compound will be paramagnetic. Complexes that simultaneously contain a fullerene radical anion and a paramagnetic metal atom have not been synthesized so far.

Studies dedicated to synthesis of dimeric and polymeric fullerene complexes, as well as transition-metal complexes with fullerene anions and radical anions, will be continued. Researchers intend to synthesize new fullerene polymers where the fullerene cages are linked through both the paramagnetic metal atom bridges and C−C bonds. Of special interest are complexes with paramagnetic fullerene radical anions, which can exhibit strong magnetic interactions and high conductivity.

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