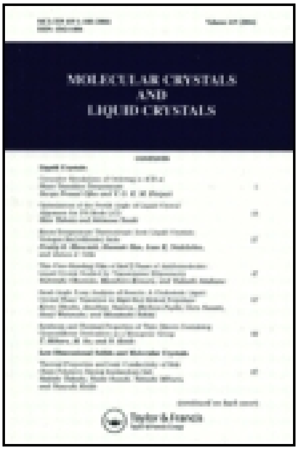

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Formation and Properties of $(C_{60}^{-})_2$ Dimers of Fullerenes Bonded by One and Two σ-Bonds in Ionic Complexes

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Formation and Properties of $(C_{60}^{-})_2$ Dimers of Fullerenes Bonded by One and Two σ-Bonds in Ionic Complexes

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New ionic complexes of fullerene C_{60}: $\{Cr^{I}(C_6H_6)_2^{\bullet+}\}\cdot(C_{60}^{\bullet-})\cdot C_6H_4Cl_2$(**1**); $\{(MDABCO^{+})\cdot Co^{II}TMPP\cdot\}_2\cdot(C_{60}^{-})_2\cdot(C_6H_4Cl_2)_{2.5}\cdot(C_6H_5CN)_{1.5}$ (**2**); *and* $(DMETEP^{+})_2\cdot(C_{60}^{-})_2\cdot\{(Mn^{II}TPP)_2\cdot DMP\}\cdot(C_6H_4Cl_2)_5$(**3**) *were obtained and studied by temperature EPR, SQUID and optical spectroscopy. Fullerene radical anions were shown to form* $(C_{60}^{-})_2$ *dimers in these complexes. The* $(C_{60}^{-})_2$ *dimer in* **1** *reversibly forms in the 160–240 K range and is bonded by one single bond (σ-dimer). According to magnetic data this dimer is diamagnetic. Complex* **2** *contains a new type of* $(C_{60}^{-})_2$ *dimer bonded by two single bonds (π-dimer). Magnetic measurements show that this dimer has about two spins per dimer and, consequently, has biradical state at 300 K. The energy gap between triplet and singlet states for this dimer was estimated to be* $70 \pm 2\,CM^{-1}$. *Complex* **3** *contains dimers of both types. The σ-dimer has 86% occupancy and the occupancy for the π-dimer is only 14%. It was shown that σ-dimer in* **3** *has the highest stability among studied ionic complexes of fullerenes and dissociates only in the 320–360 K range. The reasons for the difference in the electronic states of σ- and π-dimers of* $(C_{60}^{-})_2$ *are discussed.*

Keywords: dimerization; fullerenes; ionic complexes; magnetic properties; porphyrines

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INTRODUCTION

Ionic compounds of fullerenes manifest promising physical properties such as superconductivity and ferromagnetism [1–3]. Fullerenes also form a large variety of dimeric and polymeric structures from negatively charged anions, some of which also show interesting physical properties [4]. The existence of $(C_{60}^{-})_2$ dimers was for the first time supposed from the X-ray powder diffraction studies of the metastable phases of $M \cdot C_{60}$ ($M = K$, Rb, and Cs) obtained by doping. It was shown that such dimers are bound by one single bond and are diamagnetic [5,6]. Neutral fullerenes also form dimers. However, in contrast to negatively charged $(C_{60}^{-})_2$ dimers, the neutral $(C_{60})_2$ dimer is bound by two single bonds [7]. Azafullerene $C_{59}N$ forms the $(C_{59}N)_2$ dimer as well. In this dimer fullerene molecules are bound by one single C−C bond and such a dimer should be isoelectronic to the negatively charged $(C_{60}^{-})_2$ dimer [8].

Up to now most of the ionic complexes of fullerenes obtained by direct synthesis in solution contain only monomeric fullerene radical anions [9]. Only recently several polymeric and dimeric structures from fullerene anions have been characterized. The polymerization of $C_{60}^{\bullet-}$ radical anions was shown to occur in a ferromagnetic phase of $TDAE \cdot C_{60}$ (TDAE: tetrakis(dimethylamino)ethylene) under 7 kbar pressure. The resulted polymer is stable in ambient conditions and depolymerization is realized only above 520 K [10]. Dimerization of $C_{60}^{\bullet-}$ was found in $Cr(C_6H_5Me)_2 \cdot C_{60}$ ($Cr(C_6H_5Me)_2$: bis(toluene)chromium) at 250 K according to X-ray powder diffraction and SQUID data [11]. The molecular structure of the $(C_{60}^{-})_2$ dimers bonded by one single bond (σ-dimer), was determined from X-ray diffraction on a single crystal in ionic $Cp_2^*Cr \cdot C_{60} \cdot (C_6H_4Cl_2)_2$ (Cp_2^*Cr: decamethylchromocene) (Fig. 1*a*). Reversible dimerization occurs in this complex at 230–200 K [12]. The formation of similar dimers is also observed in several other ionic complexes of C_{60} with Cp_2Co (cobaltocene) [13], $Cr^{I}(C_6H_6)_2$ (bis(benzene)chromium) [13], $Cr(C_6H_5{-}C_6H_5)_2$(bis (diphenyl)chromium) [14] and in multi-component complexes $(Cs)_2 \cdot (C_{60})_2 \cdot CTV \cdot (DMF)_6$ (CTV: cyclotriveratrylene) [15] and $Cr(C_6H_6)_2 \cdot C_{60} \cdot [Pd(dbdtc)_2]_{0.5}$($Pd(dbdtc)_2$: dibenzyldithiocarbamate palladium (II)) [16].

In this work we summarized our recent results concerning the peculiarities of the formation of $(C_{60}^{-})_2$ dimers in ionic complexes of fullerenes. We observed unusual two-step dimerization in $\{Cr^{I}(C_6H_6)_2^{\bullet+}\} \cdot (C_{60}^{\bullet-}) \cdot C_6H_4Cl_2$(**1**)[17] (Scheme 1). New$(C_{60}^{-})_2$ dimers, bonded by two single bonds (π-dimer, Fig. 2*b*) were found in $\{Co^{II}TMPP \cdot (MDABCO^{+})\}_2 \cdot (C_{60}^{-})_2 \cdot (C_6H_4Cl_2)_{2.5} \cdot (C_6H_5CN)_{1.5}$ (**2**)

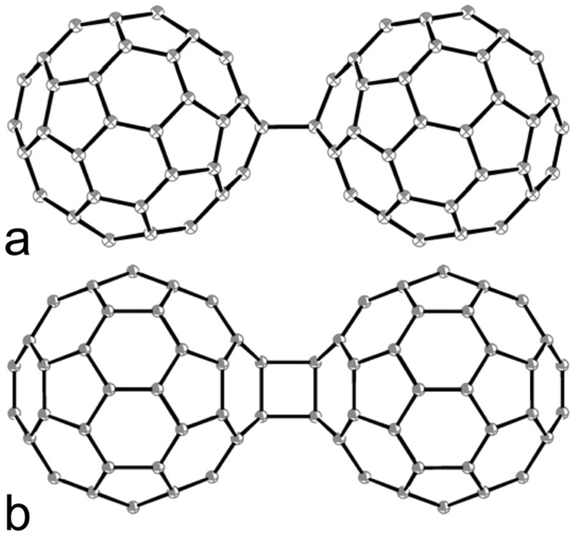
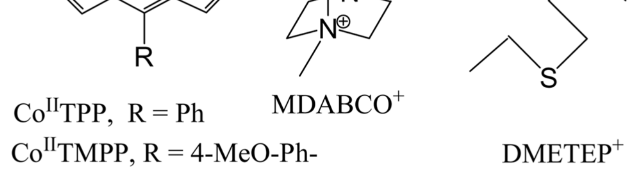


FIGURE 1 Molecular structures of negatively charged fullerene dimers: (a) σ-dimer of $(C_{60}^{-})_2$ bonded by one single bond; (b) π- dimer of $(C_{60}^{-})_2$ bonded by two single bonds.

($MDABCO^+$: cation of *N*-methyldiazabicyclooctane; TMPP: tetrakis(4-methoxyphenyl)porphyrin, Scheme 1). This dimer has an electronic state different from that of the σ-dimer and has about two electrons per a dimer at 300 K [18]. Both types of dimers coexist in (DME-



SCHEME 1 Molecular structures of the components used for preparation of fullerene complexes **1–3**.

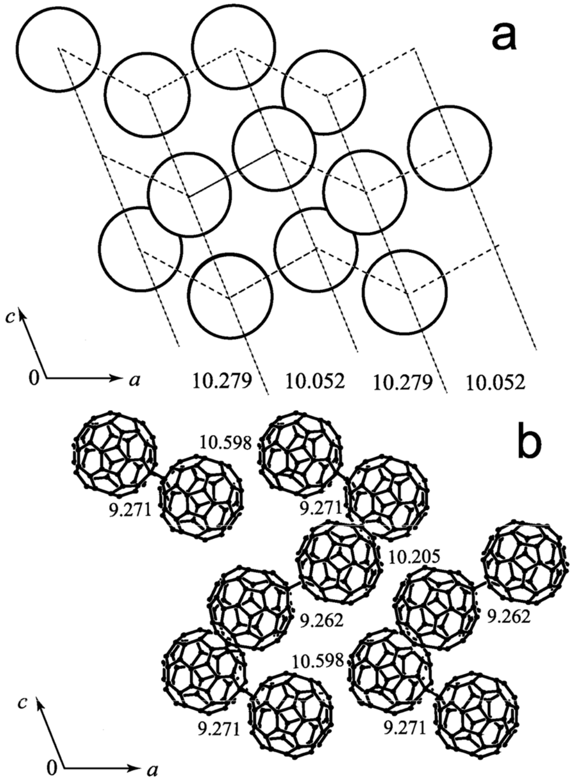


FIGURE 2 Temperature dependence of magnetic moment of polycrystalline **1** in the 1.9–300 K range. The behavior is reversible [13].

$TEP^+)_2 \cdot (C_{60}^-)_2 \cdot \{(Mn^{II}TPP)_2 \cdot DMP\} \cdot (C_6H_4Cl_2)_5$ (**3**) ($DMETEP^+$: cation of *N,N′*-dimethyl-*N*-ethylthioethylpiperazine; TPP: tetraphenylporphyrin, Scheme 1) [19]. The understanding of the difference in the electronic states of σ- and π-type fullerene dimers allows the prediction of the electronic states of other structures of fullerene anions bonded by one and two single bonds.

RESULTS AND DISCUSSION

Two-Step Dimerization in $\{Cr^I(C_6H_6)_2^{\bullet+}\} \cdot (C_{60}^{\bullet-}) \cdot C_6H_4Cl_2$(1) [17].

According to the IR- and vis-NIR spectra **1** has an ionic ground state with monomeric $C_{60}^{\bullet-}$ radical anions at room temperature (293 K) [13].

The temperature dependence of magnetic moment for **1** is shown in Figure 2. Magnetic moment is equal to 2.45 μ_B at 300 K. Therefore, both $Cr^{I}(C_6H_6)_2^{\bullet +}$ (S = 1/2) and monomeric $C_{60}^{\bullet -}$ (S = 1/2) contribute to the magnetic moment at 300 K (the calculated value is $\mu_{eff} = 2.45\,\mu_B$). Magnetic moment decreases below 240 K down to 1.73 μ_B at 160 K (Fig. 2). That indicates the disappearance of the contribution of spins from $C_{60}^{\bullet -}$ below 160 K due to their dimerization, and the magnetic moment is defined by spins localized on $Cr^{I}(C_6H_6)_2^{\bullet +}$ only (the calculated value is $\mu_{eff} = 1.73\,\mu_B$). The dimerization is accompanied by the changes in the EPR spectra. Only one Lorentzian signal is observed in the EPR spectrum of **1** at 293 K with g = 1.9913, which is an intermediate between those characteristic of $Cr^{I}(C_6H_6)_2^{\bullet +}$ (g = 1.986 [20]) and $C_{60}^{\bullet -}$ (g = 2.000–1.996 [9]). Therefore, this signal appears due to the exchange interaction between the spins of $Cr^{I}(C_6H_6)_2^{\bullet +}$ and $C_{60}^{\bullet -}$. Dimerization in the 240–160 K range shifts g-factor of the signal to 1.986, which is characteristic of $Cr^{I}(C_6H_6)_2^{\bullet +}$ [20]. That justifies the disappearance of the contribution from $C_{60}^{\bullet -}$ at dimerization. Therefore, $(C_{60}^{-})_2$ dimers bonded by one single bond are diamagnetic and EPR silent. The transition in the 240–160 K range has two peculiarities. It is relatively broad (80 K) with two well resolved steps in the temperature dependence of magnetic moment (Fig. 2). The boundary between the steps lies at about 200 K, when approximately half of dimers is formed. Such behavior can be explained if two types of dimes with different thermal stability are present in **1**.

Crystal structure of **1** was studied at 250 and 90 k. Monomeric $C_{60}^{\bullet -}$ radical anions are orientationally disordered at 250 K and are shown by circles in Figure 3a. $C_{60}^{\bullet -}$ radical anions form zigzag chains along the *a*-axis. The distances between the centers of $C_{60}^{\bullet -}$ in the chain are not uniform and equal to 10.052 and 10.279 Å (Fig. 3*a*). The former distance is shorter than the van der Waals (VdW) diameter of C_{60}(10.18 Å) and in this case shortened van der Waals C…C contacts are formed between $C_{60}^{\bullet -}$. The latter distance is long enough to prevent the formation of any shortened VdW C…C contacts. Dimerization is realized in these zigzag chains within the pairs with different distances between the centers of $C_{60}^{\bullet -}$ (Fig. 3*b*). As a result, two crystallographically independent $(C_{60}^{-})_2$ dimers are formed in the dimeric phase with interfullerene center-to-center distances of 9.262 and 9.271 Å and the lengths of interfullerene C–C single bond of 1.585(5) and 1.595(5) Å, at the dimerization from the $C_{60}^{\bullet -}$ pairs with short and long center-to-center distances, respectively. Most probably namely the structural differentiation of the $C_{60}^{\bullet -}$ pairs in the monomeric phase, in which dimerization is realized, provides a two-step dimerization process observed in magnetic measurements. Taking into account that 10.279 Å center-to-center distance is too long for the

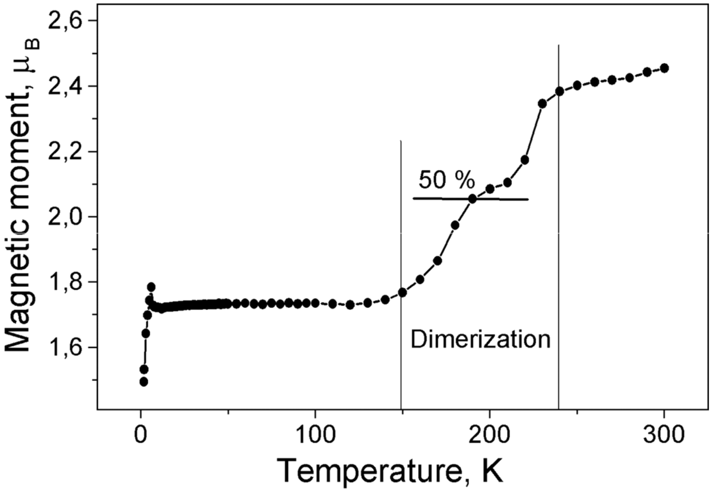


FIGURE 3 The projection ofcrystal structure of **1** along the *b*-axis: monomeric phase at 250 (a) and dimeric phase at 90 K (b) [17]. $C_{60}^{\bullet -}$ radical-anions are rotationally disordered in monomeric phase and shown by circles. The distances between the centers of fullerene anions are marked for both phases.

dimerization we can assume that on the first step (240–200 K) dimerization is realized only in the $C_{60}^{\bullet -}$ pairs with the 10.052 Å distance. The shrink of the lattice on the first step provides the possibility for the dimerization of $C_{60}^{\bullet -}$ in the pairs with the 10.279 Å distance at 200–160 K.

The formation of π-$(C_{60}^{-})_2$ Dimer in $\{(MDABCO^{+})\cdot Co^{II}TMPP\}_2\cdot(C_{60}^{-})_2\cdot(C_6H_4Cl_2)_{2.5}\cdot(C_6H_5CN)_{1.5}$(2) [18].

Complex **2** containing the π-dimer was obtained using a multi-component approach, in which neutral Co^{II}TMPP molecule was introduced in the $(MDABCO^{+})\cdot(C_{60}^{-})$ salt due to the formation of Co(Co^{II}TMPP)-N($MDABCO^{+}$) coordination bonds of 2.385(3) Å) length. The resulting $(MDABCO^{+})\cdot Co^{II}$TMPP coordination cation (Fig. 4) forms a complex with $C_{60}^{\bullet -}$. The 2:1 molar ratio between $MDABCO^{+}$ cations and the π-dimer provide formal 2 − charge on the dimer: $(C_{60}^{-})_2$. The IR-vis-NIR spectra of **2** justify this supposition [18].

Crystal structure of **2** was studied at 120 K. The C_{60}^{-} anions in the dimer are bound by two single C−C bonds of 1.581(3) Å length. These bonds are longer than those in the neutral $(C_{60})_2$dimer(1.575(7) Å [7]),

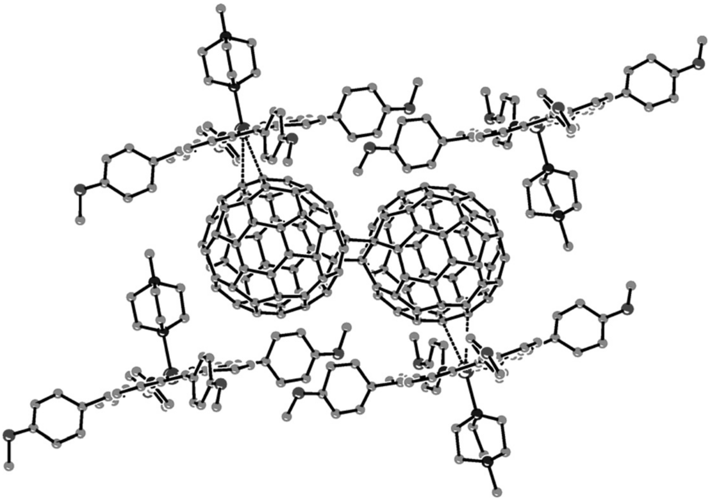


FIGURE 4 Fragment of the crystal structure of **2** at 120 K [18]. π-dimer of (C_{60}^{-})$_2$ and a "cage" from four molecules of Co^{II}TMPP coordinating MDABCO$^+$ cations by uncharged nitrogen atom are shown.

but slightly shorter than the lengths of these bonds in two different σ-(C_{60}^{-})$_2$ dimers formed in **1** (1.585(5) and 1.595(5) Å). The distance between the centers of C_{60}^{-} in the π-dimer is 9.07 Å, whereas these distances are noticeably longer in the σ-dimers formed in **1** (9.262 and 9.271 Å). It is interesting that there is no coordination between Co^{II}TMPP and π-(C_{60}^{-})$_2$ dimer in spite of that they approach close to each other. The shortest Co...C(π-(C_{60}^{-})$_2$) distances in **2** are 2.75–2.97 Å being essentially longer than the length of coordination bonds in the diamagnetic {Co^{II}TPP · (C_{60}^{-})} anions (2.28–2.32 Å [21]) and close to the length of the Co...C contacts in the neutral complexes of Co^{II}TPP with fullerenes (2.69–2.75 Å [21]). Nevertheless, the effective interaction of π-systems of Co^{II}TMPP and π-(C_{60}^{-})$_2$ dimers observed in **2** provides strong magnetic exchange interaction between them. Each π-(C_{60}^{-})$_2$ dimer is located in the cage formed by six (MDABCO$^+$) · Co^{II}TMPP units, which completely isolate dimers from each other. Probably, namely this cage can perform as a pressure cell to assist the formation of more compact π-dimer instead of generally observed σ-dimer.

Both Co^{II}TMPP and π-(C_{60}^{-})$_2$ dimers make the contribution to magnetic susceptibility of **2**. Magnetic moment of 3.47 μ_B is close to the value of magnetic moment calculated for the system of four non-interacting S = 1/2 spins per formula unit ($\mu_{eff} = 3.46\ \mu_B$). Therefore, each

C_{60}^{-} anion has about one (S = 1/2) spin at 300 K. Since these anions form one dimer, the dimer should have biradical state at 300 K with approximately two spins per dimer (S = 1). EPR data justify the presence of spins on Co^{II}TMPP (a broad signal with $g = 2.2638$ and $\Delta H = 30$ mT at 19 K) and on π-$(C_{60}^{-})_2$dimer (a narrow signal with $g = 1.9970$ and $\Delta H = 2.8$ mT at 19 K). Due to the strong exchange interaction between Co^{II}TMPP and π-$(C_{60}^{-})_2$, both signals have pure Lorentzian shape and manifest no individual features such as asymmetry or triplet splitting. The intensity of the EPR signal from π-$(C_{60}^{-})_2$ decreases with temperature. The observed temperature dependence can be described within the model of triplet state with excited triplet (S = 1) and ground singlet levels (S = 0) [22]. The energy gap between triplet and singlet levels estimated from fitting the experimental data within this model was $70 \pm 2\,\mathrm{cm}^{-1}$.

The Formation of σ- and π-Dimers in $(DMETEP^{+})_2 \cdot (C_{60}^{-})_2 \cdot \{(Mn^{II}TPP)_2 \cdot DMP\} \cdot (C_6H_4Cl_2)_5$(3) [19].

For the preparation of **3**, $(DMETEP^{+}) \cdot (C_{60}^{-})$ was crystallized with the $(Mn^{II}TPP)_2 \cdot DMP$ coordination assembly. Crystal structure of **3** was studied at 100 K. The main structural motif of **3** is the channels occupied by the zigzag chains of alternating $(C_{60}^{-})_2$ dimers and $DMETEP^{+}$ cations. The walls of the channels are built from the $(Mn^{II}TPP)_2 \cdot DMP$ units (two such channels are shown in Fig. 5). The position of the $(C_{60}^{-})_2$ dimer is occupied by two types of dimers. The σ-dimer has 86% occupancy, whereas the π-dimer has only 14% occupancy. The geometric parameters of the fullerene dimers formed in **3** are close to those obtained earlier for σ- and π-dimers in **1** and **2**.

Magnetic moment of **3** is equal to $8.3\,\mu_B$ in the 40–320 K range that is close to the contribution of two Mn(II) atoms in high (S = 5/2) spin state (the calculated magnetic moment $\mu_{eff} = 8.37\,\mu_B$). The contribution of $C_{60}^{\bullet-}$ to the magnetic moment of **3** is absent at 40–320 K due to the dimerization. Though the π-dimers are paramagnetic, their contribution to magnetic moment is small against a background of two high spin Mn(II) due to low occupancy for the dimer (this contribution cannot exceed $0.06\,\mu_B$). Above 320 K magnetic moment begins to increase up to $8.66\,\mu_B$ (360 K). That corresponds to the appearance of two S = 1/2 spins from the $C_{60}^{\bullet-}$ radical anions due to the dissociation the $(C_{60}^{-})_2$ dimers (the calculated magnetic moment is $\mu_{eff} = 8.72\,\mu_B$). Dissociation of the $(C_{60}^{-})_2$ dimers results in strong changes in the EPR spectrum of **3**. The dimeric phase manifests a complicate EPR signal with features spread over the whole magnetic field range (from

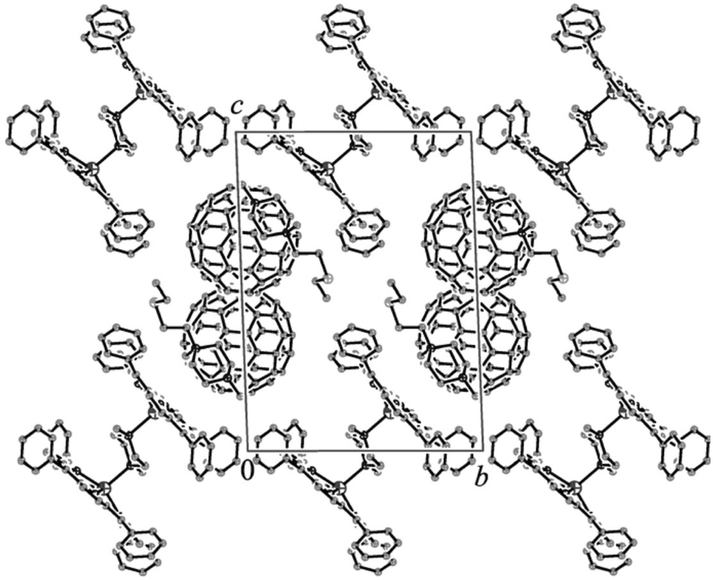


FIGURE 5 The projection of crystal structure of **3** along the *a*-axis and zigzag chains of alternating $(C_{60}^{-})_2$ dimers and DMETEP$^+$ cations [19]. Coordination $(Mn^{II}TPP)_2{\cdot}DMP$ assemblies are bonded by bidentant *N,N′*-dimethylpiperazine ligand (DMP).

0 to 700 mT). Such spectrum is associated with the presence of exchange interaction between two Mn(II) in the $(Mn^{II}TPP)_2 \cdot DMP$ coordination assemblies. At the dissociation of $(C_{60}^{-})_2$ dimers in the 320–360 K range, a new Lorentzian signal appeared with g = 2.0179 (ΔH = 65.5 mT), whereas the signal characteristic of the dimeric phase nearly disappeared at 360 K. Most probably the new signal can be attributed to two paramagnetic species $(Mn^{II}TPP)_2 \cdot DMP$ and $C_{60}^{\bullet -}$, which have exchange magnetic interaction to each other.

Temperature of the beginning of dissociation of $(C_{60}^{-})_2$ in **3** is the highest among all σ-dimers studied up to now (130–250 K [12,13,15,16]). In this context the appearance of small amount of π-dimers is expected in **3**. Stability of the $(C_{60}^{-})_2$ dimers is defined to a greater extent by their environment from cations, solvent molecules and neutral components (in the multi-component complexes) due to that the dissociation of the dimers essentially extend the space occupied by two C_{60}^{-} anions. Environment takes a role of “pressure”, which can stabilize dimers affecting their dissociation temperature. That can explain why temperatures of the beginning of dissociation vary in different ionic complexes from 130 up to 320 K. The increase of this "pressure" not only stabilizes the σ-dimers but increases the content of the π-dimers, which are more compact than the σ-dimers (the center-to-center distance between C_{60}^- anions in the dimer are 9.07 and 9.26–9.27 Å, respectively). In the limiting case the formation of the phase with π-dimers only is possible as in **2**.

CONCLUSIONS

The work shows that the fullerene radical anions can form dimers of two types in ionic complexes and salts. Generally the formation of σ-$(C_{60}^-)_2$ dimers bonded by one single bond is observed. Most probably electron from LUMO of $C_{60}^{\bullet-}$ is involved in the formation of the inter-fullerene C–C bond and due to their pairing the resulting σ-$(C_{60}^-)_2$ dimers are diamagnetic and EPR silent. The presence of two closely located negative charges on the σ-dimers and their repulsion provide relatively low stability of the interfullerene C–C bond and dimers dissociate in the 130–320 K range. Indeed, isoelectronic neutral dimer of azafullerene $(C_{59}N)_2$ is essentially higher stable than the σ-$(C_{60}^-)_2$ dimer and begins to dissociate only above 500 K [8]. External factors such as environment and initial distances between $C_{60}^{\bullet-}$ in the monomeric phase also affect stability of the dimers. Even in the same compound, when dimerization is realized in the $C_{60}^{\bullet-}$ pairs with different center-to-center distances and environment from cations and solvent molecules, two σ-$(C_{60}^-)_2$ dimers with different geometric parameters and thermal stability are formed.

The π-$(C_{60}^-)_2$ dimer bonded by two single bonds has electron state completely different from that of diamagnetic σ-dimer and manifests about two spins per dimer at 300 K. This deference is most probably associated with different mechanisms of the formation of these dimers. In contrast to σ-dimer, π-dimer should form *via* the $[2+2]$ cycloaddition reaction: two π-bonds open and two new σ-bonds form. Neutral $(C_{60}^-)_2$ dimer is also bound by two single bonds and form by similar $[2+2]$ cycloaddition reaction [7]. Since starting $C_{60}^{\bullet-}$ radical anion has 61 electrons on π-orbitals, the formation of two new single bonds in the π-dimer reduces the number of π-electrons in C_{60}^- down to 59. The odd number of π-electrons provides paramagnetism of π-dimers. However, the formation of only one bond in the σ-dimer reduces the number of π-electrons in the C_{60}^- at the dimerization down to 60 (an even number π-electrons provides diamagnetism of σ-dimers). The difference in the electronic states of σ- and π-dimers indicates that other dimeric and polymeric structures from negatively charged fullerenes bonded by one and two single bonds should also have different electronic states. For example, the formation of linear polymers $(C_{60}^-)_x$ in

$M \cdot C_{60}$ ($M = K$, Rb, and Cs), in which each C_{60}^{-} forms four single interfullerene C−C bonds [4–6], should preserve an odd number of π-electrons on C_{60}^{-} (57 π-electrons) and make these polymers paramagnetic (indeed there is spin on each C_{60}^{-} in these polymers and as a result polymers manifest metallic conductivity [4–6]). Two-dimensional polymer from fullerene tetraanions $(C_{60}^{4-})_x$, in which each C_{60}^{4-} forms four single interfullerene C−C bonds, should have an even number of π-electrons (60 π-electrons) and be diamagnetic [4].

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