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Negatively Charged π-$(C_{60}{}^{-})_2$ Dimer with Biradical State at Room Temperature

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Neutral and negatively charged fullerenes form a variety of dimeric and polymeric structures, some of which show high-temperature magnetism and metallic conductivity.[1] Neutral fullerenes form $(C_{60})_2$ dimers,[2] one-dimensional orthorhombic, and two-dimensional rhombohedral $(C_{60})_x$ polymers[3] bonded by two interfullerene σ-bonds through the [2 + 2] addition (π-structures). The $C_{60}{}^{\bullet-}$ radical anions also polymerize through the [2 + 2] addition to form linear $(C_{60}{}^{-})_x$ polymers in $M{\cdot}C_{60}$ salts (M = K, Rb, and Cs),[1c] which are structurally similar to the neutral orthorhombic $(C_{60})_x$ polymer.[3] Additional electrons on the LUMO of $C_{60}{}^{\bullet-}$ can also participate in the formation of interfullerene σ-bonds. Such structures are single-bonded ones, such as those previously described σ-$(C_{60}{}^{-})_2$ dimers (Figure 1a).[4] Therefore, both π- and σ-structures of fullerenes are known. However, the differences in their electronic states are not well studied.

Electrochemical or chemical reduction of neutral π-$(C_{60})_2$ dimers in solution results in the dissociation of reduced $(C_{60})_2{}^{\bullet-}$ species to C_{60} and $C_{60}{}^{\bullet-}$.[2] That does not allow the characterization of π-$(C_{60}{}^{-})_2$ dimers bonded by two σ-bonds up to now. In this work, we for the first time obtained and characterized such a dimer in the solid state (Figure 1b). Its molecular structure, IR, and UV−visible−NIR spectra and magnetic properties are discussed and compared with those of the σ-$(C_{60}{}^{-})_2$ dimer.[4]

A compound containing negatively charged π-$(C_{60}{}^{-})_2$ dimers, $\{(MDABCO^{+}){\cdot}Co^{II}TMPP\}_2{\cdot}(C_{60}{}^{-})_2{\cdot}(C_6H_4Cl_2)_{2.5}{\cdot}(C_6H_5CN)_{1.5}$ (**1**) (Co^{II}TMPP = cobalt(II)tetrakis(4-methoxyphenyl)porphyrin; $MDABCO^{+}$ = cation of methyldiazabicyclooctane), was obtained by a multicomponent approach used previously for the preparation of a variety of ionic complexes of fullerenes.[5] The composition of **1** was determined by single-crystal X-ray diffraction.

The crystal structure of **1** was studied at 120 K.[6] The 2:1 ratio between the coordinating $\{(MDABCO^{+}){\cdot}Co^{II}TMPP\}$ units and the π-$(C_{60}{}^{-})_2$ dimers implies that this dimer should have formal 2− charge. This conclusion is justified by optical data (Supporting Information). The $C_{60}{}^{-}$ anions are bonded in the π-dimer by two interfullerene single bonds of 1.581(3) Å length. These bonds are only slightly longer than those in the neutral π-$(C_{60})_2$ dimer (1.575(7) Å),[2] but shorter than that in the σ-$(C_{60}{}^{-})_2$ dimer (1.597(7) Å).[4b] The center-to-center distance of 9.07 Å between fullerene anions in the π-dimer of **1** is noticeably shorter than a similar 9.28 Å distance in the σ-dimer.[4b] The lengths of the 6−6 and 5−6 bonds in the π-$(C_{60})_2$ dimer (excluding the bonds with sp^3 carbons) are averaged to 1.395(11) and 1.448(10) Å and are close to those in the σ-$(C_{60}{}^{-})_2$ dimer.[4b]

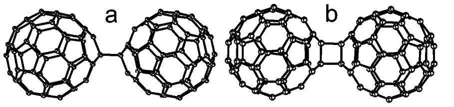

Figure 1. Perspective view of molecular structures of (a) the negatively charged σ-$(C_{60}{}^{-})_2$ dimer with C_{2h} symmetry;[4] (b) the negatively charged π-$(C_{60}{}^{-})_2$ dimer in **1** with D_{2h} symmetry according to X-ray diffraction data. Neutral π-$(C_{60})_2$ dimer[2] has a structure similar to that of the π-$(C_{60}{}^{-})_2$ dimer.

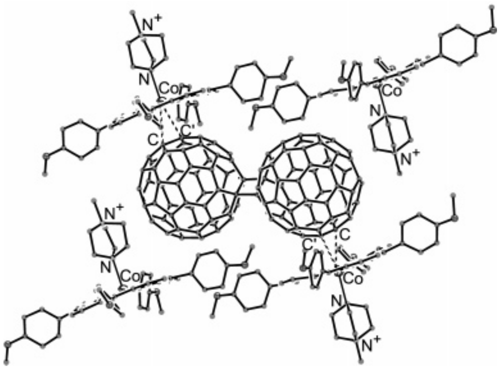

Figure 2. Fragment of crystal structure of **1** shows a cage from $\{(MDABCO^{+}){\cdot}Co^{II}TMPP\}$ units accommodating one π-$(C_{60}{}^{-})_2$ dimer. Dashed lines mark the shortened $Co{\cdots}C(\pi$-$(C_{60}{}^{-})_2)$ contacts.

The $MDABCO^{+}$ cation is a monodentate ligand and coordinates to Co^{II}TMPP by a nitrogen atom with the Co⋯N distance of 2.385(3) Å (Figure 2). Coordination σ-bonds between Co^{II}TMPP and the π-$(C_{60}{}^{-})_2$ dimers are absent in **1**, the shortest Co⋯C contacts of 2.75−2.97 Å length are noticeably longer than those in the σ-bonded $(Co^{II}TPP{\cdot}C_{60}{}^{-})$ anions (2.26−2.32 Å)[5a] and even in neutral $Co^{II}TMPP{\cdot}(C_{60})_2{\cdot}(C_6H_5CH_3)_3$ (2.65−2.67 Å).[7] Nevertheless, an effective interaction between π-systems of Co^{II}TMPP and the π-$(C_{60}{}^{-})_2$ dimers is realized in **1** (the C−C (3.26−3.32 Å) and N−C contacts (2.93−3.32 Å) are shorter than the sum of van der Waals radii of corresponding atoms). Porphyrin cages accommodate fullerene dimers in **1** and completely isolate them from one another (Figure 2). Each cage consists of six $\{(MDABCO^{+}){\cdot}Co^{II}TMPP\}$ units, two of which are in contact with the dimer by the free Co^{II}TMPP surface. Four other units are in contact with the dimer by the $MDABCO^{+}$ cations with short $C(MDABCO^{+})$−$C(\pi$-$(C_{60}{}^{-})_2)$ contacts in the 3.082−3.390 Å range (only two of four such units are shown in Figure 2 for clarity). A cage is held together by van der Waals forces and can perform as a pressure cell, which assists the formation of a more compact negatively charged π-dimer instead of σ-dimer.

Magnetic properties of **1** were studied by both SQUID and EPR techniques. It was shown that a single crystal used for the crystal structure determination and a bulky polycrystalline sample have similar temperature-dependent EPR spectra. Magnetic moment of **1** is equal to 3.47 μ_B at 300 K (Figure 3a) and is close to that calculated for a system of four noninteracting 1/2 spins (μ_{eff} = 3.46 μ_B). These spins can localize on Co^{II}TMPP and π-$(C_{60}{}^{-})_2$. Taking

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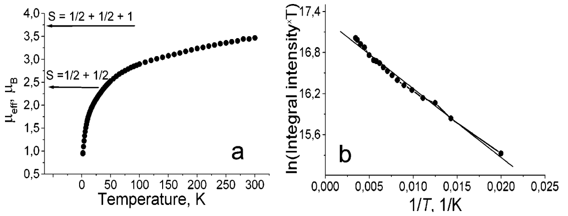
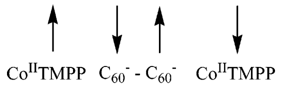


Figure 3. (a) Magnetic moment of polycrystalline **1** in the 1.9−300 K range. (b) The dependence of natural logarithm of the integral intensity of the EPR signal of the π-$(C_{60}^{-})_2$ dimer multiplied by temperature versus the inverse temperature in the 50−292 K range.

into account that the π-dimer is a single molecule, the presence of spins on both C_{60}^{-} units implies that this dimer should have a biradical state at 300 K: π-$(C_{60}^{\bullet -})_2$ ($S = 1$). Magnetic moment for a system with $S = {}^1/_2 + {}^1/_2 + 1$ is 3.74 μ_B. The presence of paramagnetic Co^{II}TMPP and π-$(C_{60}^{\bullet -})_2$ is justified by EPR since both species show individual signals. An intense narrow EPR signal with $g = 1.9997$ at room temperature, which is close to those from the radical anions of C_{60} derivatives (2.0000[8]), was attributed to the π-$(C_{60}^{\bullet -})_2$ dimer. A broad signal with $g = 2.2638$ and $\Delta H =$ 30 mT (19 K) was assigned to Co^{II}TMPP. The interaction of π-systems of Co^{II}TMPP and π-$(C_{60}^{\bullet -})_2$ dimers should provide a strong exchange interaction in the isolated Co^{II}TMPP-{π-$(C_{60}^{\bullet -})_2$}-Co^{II}TMPP chains (Figure 2). Pure Lorentzian shape of the signal from the π-$(C_{60}^{\bullet -})_2$ dimers is most probably a result of such interaction, which averages *D* and *E* parameters and leads to the disappearance of triplet features of the signal. Similarly, the signal from Co^{II}TMPP has also Lorentzian shape, despite the fact that individual Co^{II} porphyrins in the complexes with fullerenes show asymmetric EPR signals.[5a] Strong exchange interaction broadens the EPR signal from the π-$(C_{60}^{\bullet -})_2$ dimers ($\Delta H = 3.46$ mT at room temperature) relative to those of radical anions of C_{60} derivatives (0.1−0.3 mT),[8] and it remains relatively broad even at 4 K ($\Delta H =$ 1.4 mT). The *g* factor of the signal shifts with the temperature decrease to smaller values (1.9968 at 4 K). SQUID measurements for **1** justify strong antiferromagnetic exchange interactions of spins in the Co^{II}TMPP-{π-$(C_{60}^{\bullet -})_2$}-Co^{II}TMPP chains with a large negative Weiss constant of −34 K in the 35−300 K range. Magnetic moment decreases in the whole temperature range (300−1.9 K) down to $\mu_{eff} = 0.9$ μ_B at 1.9 K (Figure 3a). That can be associated with an antiferromagnetic interaction of spins in the π-$(C_{60}^{-})_2$ dimers and between Co^{II}TMPP as shown in the following scheme:



The integral intensity of the signal from the π-$(C_{60}^{-})_2$ dimer decreases with temperature from 292 down to 4 K, and this temperature dependence is simulated by a pairwise spin correlation with a ground singlet ($S = 0$) and exited triplet ($S = 1$) state. Though this model was developed for isolated pairs, it adequately describes the behavior of correlated spins, for example, in galvinoxyl crystals with an antiferromagnetic interaction of spins.[9]

$$I \propto T^{-1}\cdot\exp(-2|J_{AF}|/k_BT),\ \text{if}\ 2|J_{AF}| >> k_BT$$

J_{AF} (<0) is an antiferromagnetic exchange interaction, and $2|J_{AF}|$ corresponds to the energy gap. The plot of experimental data, $\ln(I\cdot T)$ versus $1/T$ is linear ($R = 0.994$) in the 292−50 K range (Figure 3b) and allows the estimation of $2|J_{AF}|$ value as 70±2 cm^{-1}. It is nearly 10 times smaller than the 600 and 730 cm^{-1} energy gaps estimated for the C_{60}^{2-} dianion in solution and in the solid state.[10]

The new $(C_{60}^{-})_2$ dimer in **1** bonded by two σ-bonds is the first example of a negatively charged π-dimer having a biradical state at room temperature ($S = 1$). The electronic state of this dimer is essentially different from that of the previously described σ-$(C_{60}^{-})_2$ dimer. This difference is the result of different formation mechanisms of these dimers. The π-dimer is formed by the [2 + 2] addition, and electron on the LUMO of $C_{60}^{\bullet -}$ is not involved in the bond formation. The C_{60}^{-} anions in the π-dimer retain to a great extent the properties of individual $C_{60}^{\bullet -}$ radical anions. On the contrary, the σ-$(C_{60}^{-})_2$ dimers are formed with the participation of electrons on the LUMO of $C_{60}^{\bullet -}$, which are paired, and the σ-dimers are diamagnetic.[4] According to the interfullerene bond lengths, we can expect the following order of dimer stability: σ-$(C_{60}^{-})_2$ dimer < π-$(C_{60}^{-})_2$ dimer in **1** < neutral π-$(C_{60})_2$ dimer. The σ-dimers begin to dissociate at 140−240 K.[4] The crystal structure of **1** solved at 220 K shows the retention of the π-$(C_{60}^{-})_2$ dimer. The absence of phase transitions, monotonic changes in the EPR parameters up to room temperature, and the room temperature IR spectrum justify that the π-dimer in **1** should be stable even at room temperature. However, the stability of this dimer can be associated not only with its intrinsic stability but also with the presence of a porphyrin cage, as well, which can prevent the dissociation of the dimer. The neutral π-$(C_{60})_2$ dimer decomposes in solution only above 423 K.[2]

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Supporting Information Available: Crystallographic data and crystal structure refinement of **1**, synthesis and characterization of **1**, including IR, UV−visible−NIR, EPR spectra. This material is available free of charge via Internet at http://pubs.acs.org.

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(6) Crystal data of **1**: $C_{255.5}H_{119.5}N_{13.5}Cl_5O_8Co_2$, $M_r = 3801.26$, monoclinic, $P2_1/n$, $a = 13.7980(5)$, $b = 24.3140(14)$, $c = 25.6050(15)$ Å, $\beta = 100.336(3)°$, $V = 8450.7(8)$ $Å^3$, $Z = 2$, $\rho_{calcd} = 1.494$ $g\cdot cm^{-3}$, $T =$ 120(2) K, data/parameters/restrains 15790/1458/382, $R_1 = 0.0543$, $wR_2 = 0.1433$, GOF = 1.015.

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