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Singlet-Triplet Transition in the C_{60}^{2-} Dianion

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ABSTRACT

The C_{60} complexes with decamethylcobaltocene: $(Cp^*_2Co)_2C_{60}(C_6H_4Cl_2, C_6H_5CN)_2$ (**1**) and $[K\cdot(18\text{-crown-6})]_2\cdot C_{60}\cdot(DMF)_4$ (**2**) have been obtained as single crystals by the diffusion method. The IR- and UV-VIS-NIR-spectra justify the formation of the C_{60}^{2-} dianions in these salts. EPR measurements show that the low temperature signals of **1** in the 4–140 K range and **2** in the 4–60 K range have intensity corresponding only to 0.4% and 3.5% from total C_{60}. Because of this, most of the complexes are EPR silent, and, consequently, C_{60}^{2-} has a diamagnetic

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singlet ($S = 0$) state in these temperature ranges. The appearance of a broad EPR signal in the spectum of **1** above 140 K and **2** above ~60 K is assigned to a thermal population of a close lying excited triplet ($S = 1$) state. The singlet–triplet energy gap for C_{60}^{2-} in solid **1** and **2** was estimated to be 730 ± 10 and 300 ± 10 cm^{-1}.

Key Words: Singlet-triplet transition; C_{60} Complexes; C_{60}^{2-} Dianions; EPR.

INTRODUCTION

Ionic compounds of fullerene C_{60} show interesting physical[1] and structural[2] properties. C_{60} has an unique electronic structure with three-fold degenerate LUMO (t_{1u}), which is able to accept up to 6 electrons to form anions from −1 to −6. Up to now several C_{60}^{2-} salts: PPN_2C_{60} (PPN^+: *bis*(triphenylphosphine)iminium),[3] $[K(2,2,2\text{-cryptand})]_2C_{60} \cdot (C_7H_8)_4$ (C_7H_8: toluene),[4] $(Cp^*_2Co)_2C_{60}$ and others[3] are known. In spite of this, electronic structure of the C_{60}^{2-} dianion is still under discussion. Molecular orbital calculations show that C_{60}^{2-} can have a singlet ground state with a triplet excited state and the energy gap of 300–1500 cm^{-1}.[5] The EPR study of C_{60}^{2-} in dimethyl sulfoxide (DMSO) solution shows a diamagnetic singlet ($S = 0$) ground state for this anion with a thermally populated excited triplet ($S = 1$) state and the energy gap of 600 ± 100 cm^{-1}.[6] However, the singlet–triplet energy gap for the C_{60}^{2-} anion in the solid state has not been determined yet.

This work reports on the synthesis, optical properties, and the determination of singlet–triplet energy gap for the C_{60}^{2-} anion in new ionic complexes: $(Cp^*_2Co)_2C_{60} \cdot (C_6H_4Cl_2,\ C_6H_5CN)_2$ (**1**) (Cp^*_2Co: $C_6H_4Cl_2$: decamethylcobaltocene; 1,2-dichlorobenzene; C_6H_5CN: benzonitrile) and $[K \cdot (18\text{-crown-6})]_2 \cdot C_{60} \cdot (DMF)_4$ (**2**) (DMF: *N*, *N*′-dimethylformamide).

RESULTS AND DISCUSSION

The crystals of **1** were prepared in anaerobic conditions by diffusion of *n*-hexane into the $C_6H_4Cl_2/C_6H_5CN$ (1 : 1) solution containing C_{60} and 2.4 molar equivalents of Cp^*_2Co. The composition of **1** was determined from the x-ray analysis.[7]

The crystals of **2** were obtained in anaerobic conditions by diffusion of *n*-hexane into the C_6H_6/DMF (*N*,*N*′-dimethylformamide) (1 : 1) solution containing C_{60} and three molar equvalents of K · (18-crown-6). Elemental

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analysis of **2** yields: C, % = 67.80; H, % = 4.24; N = 3.21; Calculated: C, % = 71.21; H, % = 4.82; N = 3.46; O = 15.81; K = 4.70. A lower content of C is probably associated with the addition of oxygen during elemental analysis due to air-sensitivity of this compound. The calculated values for $\mathbf{2} \cdot (O_2)_2$ are: C, % = 68.77; H, % = 4.64; N = 3.32; O = 19.00; K = 4.27.

The IR spectrum of **1** indicates the ionic ground state. The bands ascribed to C_{60} are at 1369s, 1182w, 574s, and 520w cm^{-1}. The $F_{1u}(4)$ mode of C_{60} (1429 cm^{-1} in parent fullerene) is the most sensitive to charge transfer to the fullerene molecule.[8] This mode has an intermediate position (1369 cm^{-1}) between those for -1 and -3 charged C_{60} (1392 and 1363 cm^{-1}, respectively[8]), indicating approximately -2 charge on the C_{60} molecules. The -2 charged state of C_{60} is unambiguously justified by the UV-VIS-NIR spectrum of **1** in the KBr matrix by characteristic bands at 854, 963, and 1350 nm in the NIR range.[9]

The IR spectrum of **2** also indicates the ionic ground state. The bands of C_{60} appear at 1374s, 1364s (split band), 1174w, 573s, and 529w cm^{-1}. The UV-VIS-NIR spectrum of **2** in the KBr matrix is identical to that of **1**. The bands at 854, 954, and 1320 nm in the NIR range justify the formation of C_{60}^{2-}. The absence of bands in the NIR range is characteristic of C_{60}^{-} and C_{60}^{3-} indicating the absence of these anions in **1** and **2**.

The EPR spectrum of **1** at 290 K (RT) has one broad single line ($g = 2.0006$ and the line half-width $\Delta H = 5.6$ mT, signal **I**) overlapped with a weak and narrow signal **III** (Fig. 1). The total integral intensity of signal **I** reversibly increases with temperature in the 140–290 K range [Fig. 2(a)]. Therefore, the signal **I** is attributed to the thermally-populated excited triplet ($S = 1$) state of C_{60}^{2-}. The signal has unresolved low zero-field splitting ($D \cong 0$). This corresponds to a triplet state in which two unpaired electrons with parallel spins are sufficiently separated from each other and their interaction is not reflected in the EPR spectrum.[3,6] The temperature decrease from 290 down to 140 K results in both the shift of the g-factor to larger values and the narrowing of the signal to $g = 2.0016$ and $\Delta H = 0.5$ mT [Fig. 2(b), (c)]. The integral intensity of the signal **I** at RT corresponds to ~6% population of the excited triplet state. The plot of ln (integral intensity $\times$ T) vs. $1/T$ is linear in the 290–140 K range [Fig. 2(a)] and the slope of this plot affords the singlet–triplet energy gap of 730 $\pm$ 10 cm^{-1} for C_{60}^{2-} in solid **1**.

Below 140 K (indicated by T in Fig. 2), the signal **I** is not resolved and only weak narrow signal **II** is observed down to 4 K. The behavior of the signal **II** in the 140–4 K range allows it to be distinguished from the signal **I**. The intensity of the signal **II** increases with the temperature decrease. The plot of ln (integral intensity $\times$ T) vs. $1/T$ is nearly constant showing a paramagnetic dependency [Fig. 2(a)]. The g-factor shifts to smaller values ($g = 2.0009$ at 4 K) and ΔH remains constant (0.5 mT) down to 4 K [Fig. 2(b), (c)]. Moreover,

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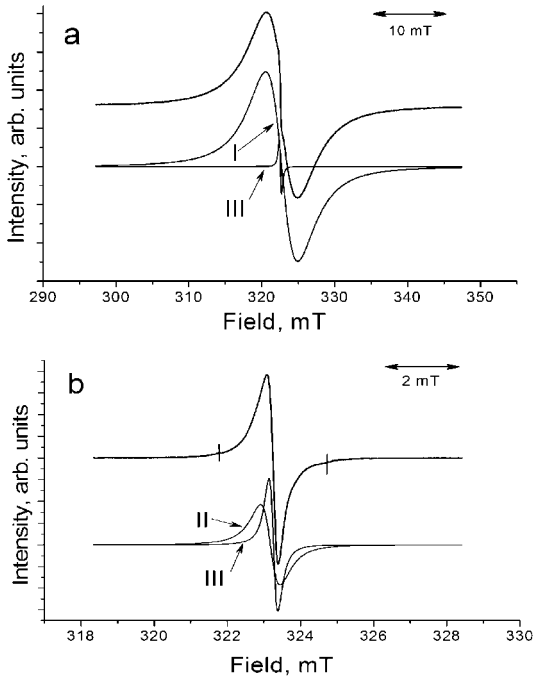

Figure 1. The EPR signals from **1** (a) at RT (290 K) and (b) 50 K. The simulation of the signals by two Lorentzian lines is shown below.

this signal is superimposed on a weak signal with the splitting of 2.77 mT at $T < 100$ K. In the 140–4 K range the signal **II** cannot be attributed to the thermally-populated excited triplet state of C_{60}^{2-} and the integral intensity of this signal (about 0.3% of the total C_{60}) is too small for the ground state of C_{60}^{2-}. Probably the signal **II** originates from a small amount of the C_{60}^{2-} spins trapped on the defects.

Weak narrow signal **III** observed from 290 down to 4 K [Fig. 1(a), (b)] can be attributed to the reduction of the $C_{120}O$ impurity.[10] Its integral intensity corresponds to 0.1% of total C_{60} and the parameters ($g = 2.0008$, $\Delta H = 0.2$ mT at RT) are almost temperature independent.

The EPR behavior of **2** is similar to that of **1**. Only broad single Lorenzian line with $g = 2.0011$ and ΔH of 2.2 mT (signal **I**) is observed at RT. Weak narrow signal **III** observed in the EPR spectrum of **1** and attributed to $C_{120}O$ impurity was not observed in **2**. The integral intensity of signal **I** increases with temperature in the 60–290 K range [Fig. 3(a)]. This allows the signal **I** in **2** to be also attributed to the thermally-populated excited triplet ($S = 1$) state

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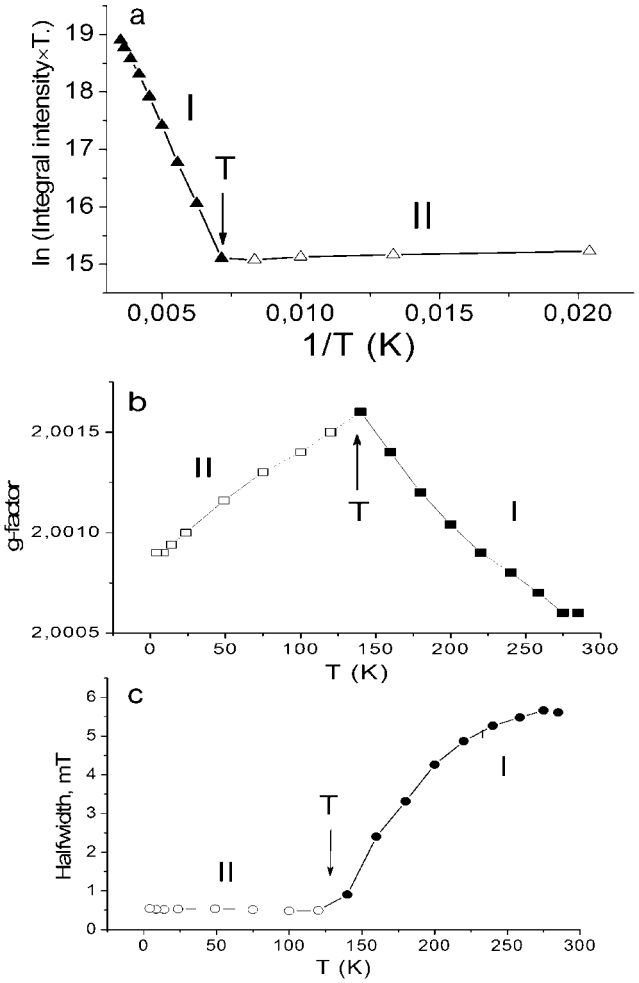

Figure 2. The temperature dependencies for EPR signals from **1** (signal **I** in the 290–140 K range and signal **II** in the 140–4 K range): (a) ln (integral intensity $\times$ T) vs. $1/T$; (b) g-factor; (c) the line halfwidth.

of C_{60}^{2-}. The temperature decrease from 290 down to 60 K results in both the shift of the g-factor to larger values and the essential narrowing of the signal **I** to $g = 2.0046$ and $\Delta H = 0.2$ mT at 50 K [Fig. 3(b), (c)]. The integral intensity of the signal **I** at RT corresponds to $\sim$12% population of the excited triplet state. The plot of ln (integral intensity $\times$ T) vs. $1/T$ is linear in the 290–160 K

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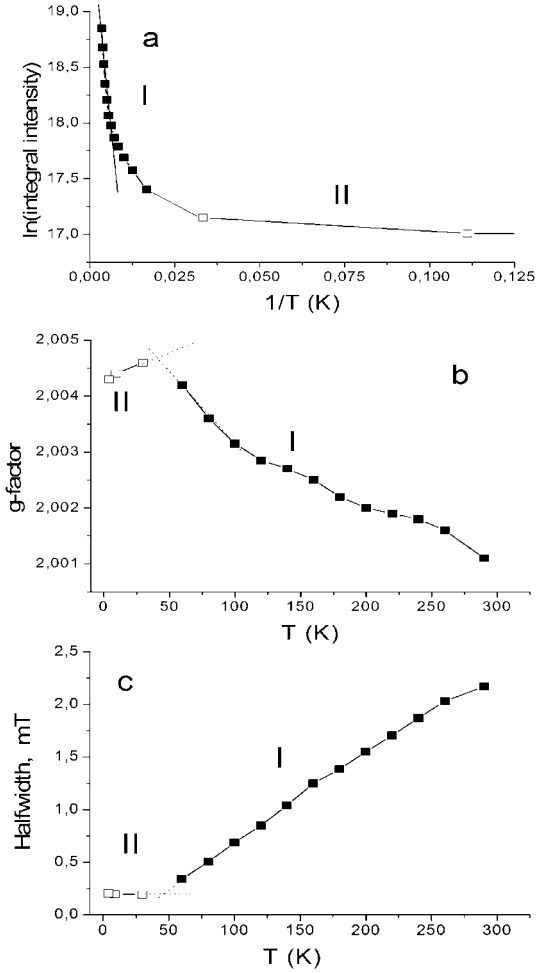

Figure 3. The temperature dependencies for EPR signals from **2** (signal **I** in the 290–60 K range and signal **II** in the 60–4 K range): (a) ln (integral intensity $\times$ T) vs. $1/T$; (b) g-factor; (c) the line halfwidth.

range [Fig. 2(a)] and the slope of this plot affords the singlet–triplet energy gap of 300 $\pm$ 10 cm^{-1} for C_{60}^{2-} in solid **2**. Below 50 K the total integral intensity of the remaining signal **II** is only 3.5% from total C_{60} (this value is essentially larger than 0.3% for the signal **II** in **1**). The integral intensity of signal **II** increases with the temperature decrease since it cannot be attributed to the thermally-populated excited triplet state of C_{60}^{2-} and is most probably

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associated with impurities. Signal **II** has nearly temperature independent ΔH of 0.2 mT and the *g*-factor shifts to smaller values with the temperature decrease down to 4 K. A similar behavior is manifested by signal **II** of **1** in the 4–140 K range.

The EPR behavior of solid **1** and **2** is qualitatively similar to that of electrochemically generated C_{60}^{2-} in the DMSO solution. Only narrow line with $\Delta H = 0.2$ mT superimposed on the split weak signal is observed at low temperatures (4.5–130 K). The intensity of these signals was calculated to be less than 4% of total C_{60}. The broad Lorentzian signal with $\Delta H = 3$ mT appears above 135 K. This signal was attributed to the thermally-populated excited triplet state, which has about 6% occupancy at 255 K. The singlet–triplet energy gap for C_{60}^{2-} in solution was determined to be 600 cm^{-1}.[6]

Thus, the EPR data show that C_{60}^{2-} in solid **1** and **2** has a diamagnetic ground state ($S = 0$) at 2–140 K for **1** and 4–60 K for **2**. A small amount of spins observed at low temperatures (0.4% and 3.5% of total C_{60}) is most probably associated with defects or impurities. Similar low-temperature narrow signals were observed for C_{60}^{2-} in solution[6] and solid PPN_2C_{60}.[3] The broad signals attributed to the thermal population of the excited triplet state ($S = 1$) of C_{60}^{2-} in **1** and **2** appear above 140 and 60 K. Such signals were previously observed only in solution[6] and were not found in solid PPN_2C_{60}.[3] The singlet–triplet energy gap for C_{60}^{2-} in solid **1** and **2** was estimated to be 730 $\pm$ 10 and 300 $\pm$ 10 cm^{-1}. The population of the exited triplet state attains 6% and 12% for **1** and **2** at RT. It could be observed that the smaller singlet–triplet energy gap in **2** results in smaller temperature of the appearance of a broad triplet signal and larger population of excited triplet state at RT relative to those in **1** and C_{60}^{2-} in DMSO solution.[6] The signals attributed to the triplet state are broad at RT and narrow with the temperature decrease as EPR signals from $C_{60}^{\cdot-}$ and C_{60}^{3-}.[10] However, in contrast to these signals, the integral intensity of the triplet signal in **1** and **2** decreases with temperature.

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