

The formation of single-bonded $(C_{60})_2$ and $(C_{70})_2$ dimers in ionic complexes of fullerenes

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Abstract

New ionic complexes of fullerenes C_{60} and C_{70} : $Cp^*_2Cr-C_{60}(C_6H_4Cl_2)_2$ (**1**) and $Cs_2(C_{70})_2\cdot CTV\cdot (DMF)_7\cdot (C_6H_6)_{0.75}$ (**2**) (Cp^*_2Cr : decamethylchromocene; CTV: cyclotrimeratrylene) have been obtained as single crystals. It is shown that paramagnetic fullerene radical anions form diamagnetic single-bonded $(C_{60})_2$ and $(C_{70})_2$ dimers in both complexes at low temperatures, the molecular structures of which are presented. The dimer-monomer phase transitions at 200–220 K in **1** (reversible) and at 360–390 K in **2** are discussed.

Keywords: Fullerenes C_{60} and C_{70} , Ionic complexes, Dimers, X-ray diffraction, Electron paramagnetic resonance, SQUID measurements

Ionic compounds of fullerenes are interesting not only by their physical properties [1, 2] but the large variety of dimeric and polymeric structures of negatively charged fullerenes as well. By now the linear C_{60}^- and C_{60}^{3-} polymers and the two-dimensional bridged C_{60}^{4-} structures have been discovered [3]. Negatively charged fullerenes are also able to dimerize. For the first time $(C_{60})_2$ dimer was found in a metastable phase of $(Rb^+)(C_{60}^-)$ [4]. Recently, the dimerization of C_{60}^- was observed in ionic $(ToI_2Cr^+)(C_{60}^-)$ (ToI_2Cr : bis(toluen)chromium) at 250K [5]. However, in both cases the compounds were obtained only as powder. The preparation of new ionic complexes: $(Cp^*_2Cr^+)(C_{60}^-)$ $(C_6H_4Cl_2)_2$ (**1**) (Cp^*_2Cr : decamethylchromocene; and $C_6H_4Cl_2$: 1,2-dichlorobenzene) [6] and $(Cs^+)_2(C_{70})_2\cdot CTV\cdot (DMF)_7\cdot (C_6H_6)_{0.75}$ (**2**) (CTV: cyclotrimeratrylene; DMF: *N,N*-dimethylformamide) [7] as single crystals allows us to determine the molecular structure of single-bonded $(C_{60})_2$ and $(C_{70})_2$ dimers as well as to study the dimer-monomer phase transitions.

The crystals of **1** and **2** were obtained in anaerobic conditions by the diffusion method [6, 7]. The composition of the complexes was determined by X-ray diffraction data. Crystal data for **1**: monoclinic, $P2_1$, $a=22.973(1)$, $b=20.785(1)$, $c=24.747(1)$ Å, $\beta=106.387(3)^\circ$, $V=11247.7(9)$ Å³, $Z=2$, $\rho_{calc}=1.579$ g·cm⁻³, $T=100$ K, $R=0.051$, $wR=0.147$; for **2**: monoclinic, $P2_1/n$, $a=25.937(8)$, $b=29.113(11)$, $c=34.221(14)$ Å, $\beta=103.328(9)^\circ$, $V=25114(16)$ Å³, $Z=4$, $\rho_{calc}=1.568$ g·cm⁻³, $T=120$ K, $R=0.104$, $wR=0.262$.

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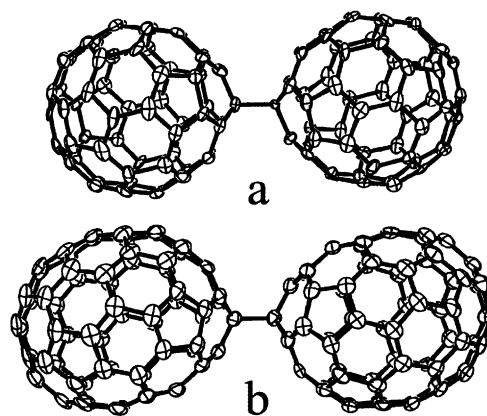


Fig. 1. Molecular structure of $(C_{60})_2$ (a) and $(C_{70})_2$ (b) dimers in **1** and **2**.

Results and Discussion

According to X-ray diffraction data at 100K for **1** [6] C_{60}^- forms single-bonded $(C_{60})_2$ dimers (Fig. 1a). The $(C_{60})_2$ configuration has C_{2h} symmetry, as was predicted from calculations [8]. The length of the intercage C–C bond (1.597(7) Å) is longer than the normal C–C bond between sp^3 carbons (1.541(3) Å) but close to the predicted one (1.618 Å) [8]. The intercage center-to-center distance in the dimer is equal to 9.28 Å.

In the structure of **2** [7] C_{70}^- also forms single-bonded $(C_{70})_2$ dimers at 120K (Fig. 1 b). The symmetry of $(C_{70})_2$ configuration is also close to C_{2h} . This symmetry is lower than D_{5h} symmetry of the parent C_{70} . The bond length of the intercage C–C bond is 1.584(9) Å. Thus, the length of

the intercage C-C bond has the tendency to decrease in the order: $(C_{60})_2$ dimer (1.597(7) Å) > $(C_{70})_2$ dimer (1.584(9) Å) > neutral $(C_{60})_2$ dimer (1.575(7) Å) [9]. The change in the length of the intercage C-C bond in the fullerene dimers is qualitatively interpreted by the on-site Coulomb repulsive energy of a dimer. This energy is maximal in the $(C_{60})_2$ dimer, decreases in the larger $(C_{70})_2$ dimer and is equal to zero in the neutral $(C_{60})_2$ dimer.

The magnetic susceptibility of **1** is measured in the 1.9–300 K range. The magnetic moment is equal to $3.88 \mu_B$ at low temperatures (50–200 K). Thus, only spins from $Cp^*_2Cr^+$ (the non-interacting $S=3/2$ system has $\mu=3.87 \mu_B$) contribute to the magnetic susceptibility. The step-like and reversible change of the magnetic moment of **1** from 3.88 to $4.20 \mu_B$ is detected in the 200–230 K range above which the magnetic moment is defined by both spins from $Cp^*_2Cr^+$ ($S=3/2$) and $C_{60}^{\cdot-}$ ($S=1/2$) (the non-interacting $S=3/2, 1/2$ system has $\mu=4.27 \mu_B$). Thus, the change of the magnetic moment of **1** indicates the appearance of the contribution of $C_{60}^{\cdot-}$ spins consistent with the dissociation of the diamagnetic $(C_{60})_2$ dimers. Complex **1** has intense EPR signal at low temperatures (4–200 K) (Fig. 2). This signal is asymmetric with g_L and $g_H=2.013$ and line half-width of $\Delta H = 5.5$ mT at 4 K. The g_L has at least 9 components probably due to the polycrystallinity of the sample. First the most intense component has $g=3.974$ and $\Delta H = 7.0$ mT and all other components shift to the smaller g -values, become broader and decrease in the intensity. The observed signal can be attributed to $Cp^*_2Cr^+$ with $S=3/2$ ground state ($g_L = 4.02$ (1) and $g_H = 2.001$ (1) for solid $(Cp^*_2Cr^+)(PF_6^-)$ [10]). By heating the sample the signal from $Cp^*_2Cr^+$ disappears at 200–220 K (Fig. 2). Since the disappearance of the EPR signal from $Cp^*_2Cr^+$ and the appearance of the magnetic moment ascribed to $C_{60}^{\cdot-}$ occur simultaneously we can conclude that the dissociation of $(C_{60})_2$ dimers in the 200–220 K range results in the transition from the odd-spin EPR active species containing paramagnetic $Cp^*_2Cr^+$ and diamagnetic $(C_{60})_2$ at low temperatures (4–200 K) to an EPR-silent, integral-spin species via a magnetic coupling between $Cp^*_2Cr^+$ and $C_{60}^{\cdot-}$ at higher temperatures (220–293 K).

The magnetic susceptibility of **2** was measured in 1.9–390 K range. The magnetic susceptibility is negative at RT and is temperature independent in 1.9–260 K range ($\chi_M = -1.7 \times 10^{-3} \text{ emu} \cdot \text{mol}^{-1}$). Thus, $(C_{70})_2$ dimers are diamagnetic. The small increase of the magnetic susceptibility observed in the 260–360 K range may be attributed to the beginning of the monomerization of $(C_{70})_2$ dimers (this is also the reason of the appearance of weak EPR signal from $C_{70}^{\cdot-}$ in the spectrum of **2** at 293 K ($g_1=2.0042$ with $\Delta H=0.8$ mT and $g_2=2.0024$ with $\Delta H=0.2$ mT). At the heating of **2** above 360 K the magnetic susceptibility increases abruptly together with the intensity of EPR signal attributed to $C_{70}^{\cdot-}$. This indicates that $(C_{70})_2$ dimers actually dissociate in 360–390 K range to $C_{70}^{\cdot-}$ radical anions (calc. by 90% at 390 K).

Thus, the temperature of the dimer-monomer transition for charged $(C_{60})_2$ and $(C_{70})_2$ and neutral $(C_{60})_2$ dimers

correlates with the length of the intercage C-C bond and increases in the order: 200–220 K for $(C_{60})_2$ dimer, 360–390 K for $(C_{70})_2$ dimer and 423–448 K for $(C_{60})_2$ dimer [9].

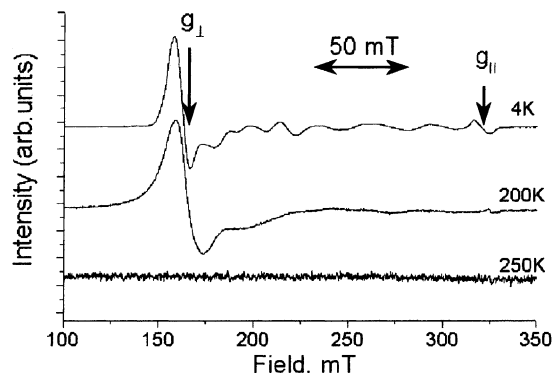


Fig. 2. EPR spectrum of **1** at 4, 200 and 250 K.

In conclusion, new ionic complexes of fullerenes C_{60} and C_{70} : $(Cp^*_2Cr^+)(C_{60}^{\cdot-})(C_6H_4Cl_2)_2$ (**1**) and $(Cs^+)_2(C_{70})_2 \cdot CTV \cdot (DMF)_7 \cdot (C_6H_6)_{0.75}$ (**2**) were obtained as single crystals. It is shown that the fullerenes form single-bonded $(C_{60})_2$ and $(C_{70})_2$ dimers at low temperatures. The length of the inter-cage C-C bond decreases in the order: $(C_{60})_2$ dimer > $(C_{70})_2$ dimer > neutral $(C_{60})_2$ dimer. The dimer-monomer phase transitions were observed at 200–220 K in **1** and at 360–390 K in **2**. The transition in **1** is reversible and is accompanied by the increase of the magnetic moment from $3.88 \mu_B$ ($S=3/2$) to $4.20 \mu_B$ ($S=3/2, 1/2$) and the disappearance of an EPR signal from $Cp^*_2Cr^+$, simultaneously. Those are the result of the dissociation of diamagnetic $(C_{60})_2$ dimers to paramagnetic $C_{60}^{\cdot-}$. The temperature of the dimer-monomer phase transition increases in the order: 200–220 K for $(C_{60})_2$ dimer, 360–390 K for $(C_{70})_2$ dimer and 423–448 K for neutral $(C_{60})_2$ dimer and correlates with the length of the intercage C-C bond.

Acknowledgments

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