The Reversible Formation of a Single-Bonded (C60−)2 Dimer in Ionic Charge Transfer Complex: Cp*2Cr·C60(C6H4Cl2)2. The Molecular Structure of (C60−)2

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Fullerenes have two most interesting features: namely, the ability to be reduced to the anions from 1− to 6−[1] and to form covalent bonds between fullerene molecules in a charged state, under pressure or irradiation.[2]

By now the quasi-one-dimensional bridged C_{60}^-, the quasi-one-dimensional bridged C_{60}^{3-} as well as the two-dimensional bridged C_{60}^{4-} structures have been discovered in fullerene salts with alkali metals.[2] C_{60} in the neutral state forms a $(C_{60})_2$ dimer.[3a] The $(C_{60}^-)_2$ dimers are only found in the metastable phase of Rb·C_{60}[3b] and in ionic Tol2Cr·C_{60} (Tol2Cr = bis(toluene)chromium)[3c], the structures of which were studied by X-ray powder diffraction. The calculations show that the single-bonded $(C_{60}^-)_2$ dimer with C_{2h} symmetry is the most stable configuration.[4]

Decamethylmetallocenes (Cp*2M^II) have a strong donor ability and can be used for the preparation of ionic complexes with fullerenes. As a result Cp*2Co is suitable for the preparation of a dianionic salt of C_{60},[5a] and Cp*2Ni yields the ionic Cp*2Ni·C_{60}·CS2.[5b] In all these complexes, the fullerene species exist in a monomeric form. In this report we describe the reversible formation of a single-bonded $(C_{60}^-)_2$ dimer in the ionic complex of C_{60} with decamethylchromocene (Cp*2Cr), the molecular structure of which was first determined by the X-ray diffraction on a single crystal.

Cp*2Cr·C60(C6H4Cl2)2 (1) was obtained under anaerobic conditions by the diffusion of hexane in 1,2-dichlorobenzene (C6H4Cl2) containing C_{60} and an equimolar amount of Cp*2Cr.

The IR spectrum of 1 at room temperature (RT) shows the ionic ground state of the complex. In 1 the $F_{1u}(4)$ C_{60} mode, which is the most sensitive to the charge transfer to fullerene molecule, shifts by 36 cm−1 relative to the starting C_{60} (1429 cm−1) to 1393 cm−1. Previously studied Rb+·C60•− salt has a position of $F_{1u}(4)$ mode close to this at 1392 cm−1.[6a] Three other C_{60} $F_{1u}(1−3)$ modes (527, 577, and 1181 cm−1, respectively) remain at their position; however, the intensity of the $F_{1u}(2)$ mode is essentially increased relative to that of $F_{1u}(1)$ mode. The bands at 437, 1021, 1380, 1434, and 1474 cm−1 are ascribed to Cp*2Cr. The shift of the band of neutral Cp*2Cr from 418 to 437 cm−1 in 1 shows the formation of Cp*2Cr+.[6b] The band with the maximum at 1080 nm is observed in the NIR spectrum of 1 measured in KBr pellet. This band is characteristic of C60•− radical anions.[1] The absence of any additional bands in the IR spectrum which usually appear with the dimerization or polymerization of fullerides[6c] indicates the monomeric state of C60•− at RT.

The RT structure of 1[7] contains orientationally disordered fullerene molecules but well-ordered Cp*2Cr+ units. The C60•− forms the uniform zigzag chains in 1 with the shortest center-to-center distance of about 10.11 Å.

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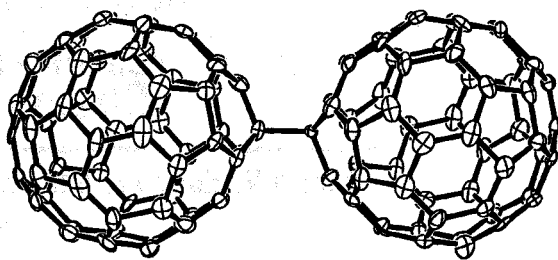**Figure 1.** ORTEP drawing of the structure of (C60−)2 dimer in 1 at 100 K.

Under cooling, a reversible structural transformation takes place at around 220 K, accompanied with the unit cell multiplication. The low-temperature (LT) structure of 1[7] was studied at 100 K. In contrast to the RT configuration, the C60•− forms single-bonded $(C_{60}^-)_2$ dimers (Figure 1). Even though a disorder in the fullerene part was still observed, the structure could be solved correctly. The disordered $(C_{60}^-)_2$ dimers are fixed in two orientations linked one to another by the rotation around the long axis of a dumbbell $(C_{60}^-)_2$ with an angle of about 142°. The occupancy factors are 0.75 and 0.25.

The $(C_{60}^-)_2$ configuration has C_{2h} symmetry, as was predicted from the calculations.[4] The average bond angle of 109° for sp3 carbons is close to the tetrahedral geometry. The length of the 6−6 and 6−5 bonds (excluding the bonds with sp3 carbons) are averaged to 1.391 (21) and 1.445 (21) Å, respectively. The length of the intercage C−C bond (1.597(7) Å) is longer than that for the normal C−C bond between sp3 carbons (1.541(3) Å)[8] but close to the predicted one (1.618 Å).[4b] The intercage center-to-center distance in the dimer is equal to 9.28 Å. For comparison, in the dimer phase of Rb·C60 this distance was found to be ~9.34 Å.[3b]

One can expect that the single-bonded $(C_{60}^-)_2$ dimer in 1 is less stable than the neutral $(C_{60})_2$ dimer where double covalent bonding of a noticeably shorter length (1.575(7) Å)[3a] occurs through [2 + 2] cycloaddition. Indeed, the dissociation temperature of the charged $(C_{60}^-)_2$ dimer, 200−220 K, is essentially lower than that of the neutral $(C_{60})_2$ dimer, 423−448 K[3a]. The estimated intercage C−C bond dissociation energy of 63 ± 4 kJ mol−1 also indicates a weakness of this bond in the $(C_{60}^-)_2$ dimer.

The whole packing of the complex may be described as a honeycomb network in which $(C_{60}^-)_2$ dimers are held together by Cp*2Cr+ cations to form large continuous channels (Figure 2). The channels pass along the [101] direction and are occupied by C6H4Cl2 solvent molecules. The dimers have several shortened contacts with each other in the columns along the [101] direction (the shortest distance = 3.266(6) Å) and C_{60} center-to-center distance between adjacent dimers = 9.91 Å) and with Cp*2Cr+ (the shortest distance = 3.049(6) Å). It should be noted that the dimer [101] columns are the result of the dimerization of the C60•− uniform zigzag chains of the RT structure.
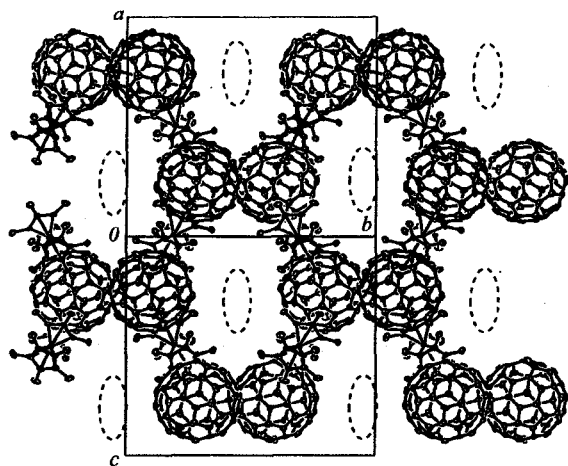
Figure 2. The crystal structure of Cp*$_2$Cr·C$_{60}$(C$_6$H$_4$Cl$_2$)$_2$ (**1**) at 100 K viewed down the [101] direction. The dimers are shown in their major orientation. The dashed ellipses show the channels containing the C$_6$H$_4$Cl$_2$ molecules, which are not shown.
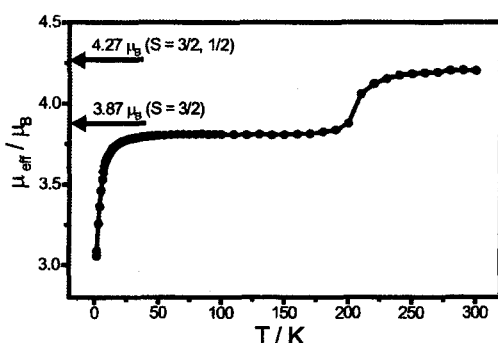

Figure 3. The dependence of the magnetic moment (μ_{eff}) vs temperature for polycrystalline **1** between 300 and 1.9 K. The behavior is reversible.

The magnetic susceptibility of **1** is measured in the 300–1.9 K range (Figure 3). The magnetic moment is equal to 4.20 μ_B at RT. Thus, both spins from Cp*$_2$Cr$^+$ ($S = {}^3/_2$) and C$_{60}{}^{\bullet-}$ ($S = {}^1/_2$) contribute to the magnetic susceptibility (the spin-only value expected for a noninteracting $S = {}^3/_2$, ${}^1/_2$ system is 4.27 μ_B). The steplike and reversible change of the magnetic moment of **1** from 4.20 to 3.88 μ_B is detected in the 230–200 K range, below which the magnetic moment is defined only by the spins from Cp*$_2$Cr$^+$ (the expected value for the noninteracting $S = {}^3/_2$ system is 3.87 μ_B). Thus, the change of the magnetic moment of **1** clearly indicates the disappearance of the contribution of C$_{60}{}^{\bullet-}$ spins consistent with the formation of the diamagnetic (C$_{60}{}^-$)$_2$ dimers. This situation is similar to that in the ionic Tol$_2$Cr·C$_{60}$ in which the dimerization of C$_{60}{}^{\bullet-}$ at 250 K results in a step decrease of the magnetic moment from 2.5 to 1.72 μ_B.[3c] The decrease of the magnetic moment of **1** at a temperature lower than 30 K (Figure 3) indicates the weak antiferromagnetic interaction between Cp*$_2$Cr$^+$ spins. The spin ordering, however, is not observed down to 1.9 K.

1 is EPR-silent at RT. By analogy with ionic Cr^{III}TPP$^+$·(C$_{60}{}^{\bullet-}$) (THF)$_3$ (CrTPP = tetraphenyl-21H,23H-porphinato chromium, and THF = tetrahydrofuran) which is also EPR-silent[9a] we can deduce that the interaction of C$_{60}{}^{\bullet-}$ with Cp*$_2$Cr$^+$ leads to an EPR-silent, integral-spin species via a magnetic coupling. By cooling the sample a new signal appears at 220–200 K in the EPR spectrum. This signal is asymmetric with $g_\perp = 3.974$ with $\Delta H = 7.0$ mT and $g_\parallel = 2.013$ with $\Delta H = 5.5$ mT at 4 K and is ambiguously ascribed to Cp*$_2$Cr$^+$ with $S = {}^3/_2$ ground state ($g_\perp = 4.02$ (**1**) and $g_\parallel = 2.001$ (**1**) for (Cp*$_2$Cr$^+$)(PF$_6{}^-$) in the solid state[6b]). The parameters

(g-factor and half-width) of the EPR signal from Cp*$_2$Cr$^+$ only weakly depend on the temperature between 4 and 200 K.

Since the appearance of the EPR signal from Cp*$_2$Cr$^+$ and the disappearance of the magnetic moment ascribed to C$_{60}{}^{\bullet-}$ occur simultaneously, we can conclude that the formation of diamagnetic (C$_{60}{}^-$)$_2$ dimers breakdowns the magnetic coupling between C$_{60}{}^{\bullet-}$ and Cp*$_2$Cr$^+$ and leads to the formation of odd-spin EPR-active species containing paramagnetic Cp*$_2$Cr$^+$ and diamagnetic (C$_{60}{}^-$)$_2$. A somewhat similar effect has been observed in the ionic TDAE$^{\bullet+}$·C$_{60}{}^{\bullet-}$ (TDAE = tetrakis(dimethylamino)ethylene) in which the polymerization of C$_{60}{}^{\bullet-}$ under pressure (>10 kbar) results in the appearance of the EPR signal from TDAE$^{\bullet+}$.[9b]

In conclusion, a new ionic complex of C$_{60}$ with decamethyl-chromocene: Cp*$_2$Cr·C$_{60}$(C$_6$H$_4$Cl$_2$)$_2$ (**1**) is obtained as single crystals. The ionic ground state of the complex is confirmed by the IR- and NIR-spectra. The fullerides are monomeric in **1** at RT, whereas they form single-bonded (C$_{60}{}^-$)$_2$ dimers at 100 K. The length of the intercage C–C bond is 1.597(7) Å, and the interfullerene distance is equal to 9.28 Å. The phase transition resulting in the C$_{60}{}^{\bullet-}$ dimerization is observed in the 220–200 K range, the transformation being reversible. The transition is accompanied by changes in the unit cell parameters, the decrease of the magnetic moment from 4.20 μ_B ($S = {}^3/_2$, ${}^1/_2$) to 3.88 μ_B ($S = {}^3/_2$), and the appearance of an EPR signal from Cp*$_2$Cr$^+$, simultaneously. The two latter effects are the result of the quenching of magnetism by the formation of diamagnetic (C$_{60}{}^-$)$_2$ dimers. The (C$_{60}{}^-$)$_2$ dimers are also formed in similar ionic Tol$_2$Cr·C$_{60}$ with short distances between the centers of C$_{60}{}^{\bullet-}$ (9.97 Å).[3c] Thus, the C$_{60}{}^{\bullet-}$ can dimerize reversibly in the ionic complexes in which the distances between C$_{60}{}^{\bullet-}$ are rather short.

Supporting Information Available: Crystallographic data and crystal structure refinement of **1** at 300 and 100 K, synthesis and characterization for **1** including IR, UV–visible–NIR, EPR, and SQUID (PDF). This material is available free of charge via Internet at http://pubs.acs.org.

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(7) Crystallographic data: (1) 300 K: C$_{92}$H$_{38}$Cl$_4$Cr$_1$, black, monoclinic, C2/c, $a = 23.167(5)$ Å, $b = 20.983(5)$ Å, $c = 14.609(2)$ Å, $\beta = 123.415(8)°$, $V = 5928.(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.498$ g·cm^{-3}. (2) 100 K: C$_{368}$H$_{152}$Cl$_{16}$-Cr$_4$, monoclinic, $P2_1$, $a = 22.973(1)$ Å, $b = 20.785(1)$ Å, $c = 24.747(1)$ Å, $\beta = 106.387(3)°$, $V = 11247.7(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.579$ g·cm^{-3}. $R(F_o) = 0.051$, $wR(F_o^2) = 0.147$, and GOF = 1.013

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