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The Reversible Formation of a Single-Bonded $(C_{60}^{-})_2$ Dimer in Ionic Charge Transfer Complex: $Cp^*_2Cr{\cdot}C_{60}(C_6H_4Cl_2)_2$. The Molecular Structure of $(C_{60}^{-})_2$

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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 $Rb{\cdot}C_{60}$[3b] and in ionic $Tol_2Cr{\cdot}C_{60}$ (Tol_2Cr = 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 $Cp^*_2Ni{\cdot}C_{60}{\cdot}CS_2$.[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.

$Cp^*_2Cr{\cdot}C_{60}(C_6H_4Cl_2)_2$ (**1**) was obtained under anaerobic conditions by the diffusion of hexane in 1,2-dichlorobenzene ($C_6H_4Cl_2$) 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 $Rb^{+}{\cdot}C_{60}^{\bullet -}$ 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 $C_{60}^{\bullet -}$ 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 $C_{60}^{\bullet -}$ at RT.

The RT structure of **1**[7] contains orientationally disordered fullerene molecules but well-ordered $Cp^*_2Cr^{+}$ units. The $C_{60}^{\bullet -}$ forms the uniform zigzag chains in **1** with the shortest center-to-center distance of about 10.11 Å.

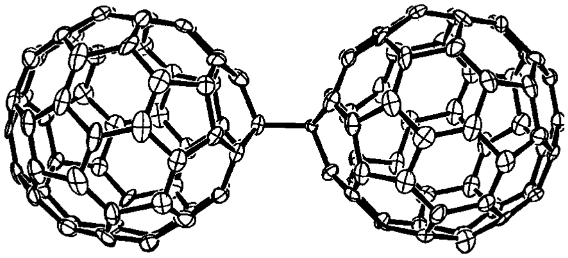

Figure 1. ORTEP drawing of the structure of $(C_{60}^{-})_2$ dimer in **1** at 100 K.

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 $C_{60}^{\bullet -}$ 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 sp^3 carbons is close to the tetrahedral geometry. The length of the 6−6 and 6−5 bonds (excluding the bonds with sp^3 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 sp^3 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 $Rb{\cdot}C_{60}$ 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 $C_6H_4Cl_2$ 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 $C_{60}^{\bullet -}$ uniform zigzag chains of the RT structure.

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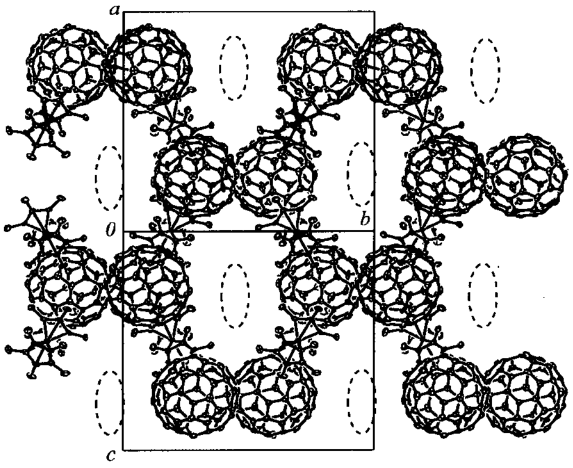

Figure 2. The crystal structure of $Cp^*_2Cr{\cdot}C_{60}(C_6H_4Cl_2)_2$ (**1**) at 100 K viewed down the [101] direction. The dimers are shown in their major orientation. The dashed ellipses show the channels containing the $C_6H_4Cl_2$ molecules, which are not shown.

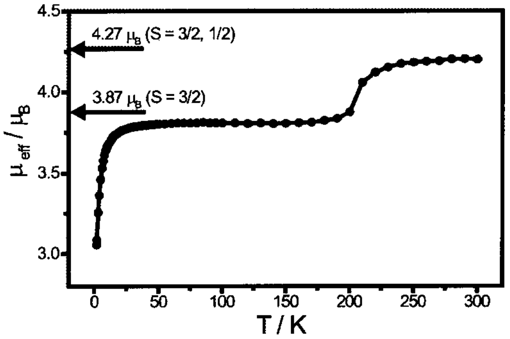

Figure 3. The dependence of the magnetic moment (μ_{eff}) vs temperature for polycrystalline **1** between 300 and 1.9 K. The behavior is reversible.

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 $Cp^*_2Cr^+$ ($S = {}^3/_2$) 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 $Cp^*_2Cr^+$ (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 $Tol_2Cr{\cdot}C_{60}$ 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 $Cp^*_2Cr^+$ spins. The spin ordering, however, is not observed down to 1.9 K.

1 is EPR-silent at RT. By analogy with ionic $Cr^{III}TPP^+{\cdot}(C_{60}^{\bullet -})(THF)_3$ (CrTPP = tetraphenyl-21*H*,23*H*-porphinato chromium, and THF = tetrahydrofuran) which is also EPR-silent[9a] we can deduce that the interaction of $C_{60}^{\bullet -}$ with $Cp^*_2Cr^+$ 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 $Cp^*_2Cr^+$ with $S = {}^3/_2$ ground state ($g_\perp = 4.02$ (1) and $g_\parallel = 2.001$ (1) for $(Cp^*_2Cr^+)(PF_6^-)$ in the solid state[6b]). The parameters (*g*-factor and half-width) of the EPR signal from $Cp^*_2Cr^+$ only weakly depend on the temperature between 4 and 200 K.

Since the appearance of the EPR signal from $Cp^*_2Cr^+$ 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 $Cp^*_2Cr^+$ and leads to the formation of odd-spin EPR-active species containing paramagnetic $Cp^*_2Cr^+$ and diamagnetic $(C_{60}^-)_2$. A somewhat similar effect has been observed in the ionic $TDAE^{\bullet +}{\cdot}C_{60}^{\bullet -}$ (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 decamethylchromocene: $Cp^*_2Cr{\cdot}C_{60}(C_6H_4Cl_2)_2$ (**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 $Cp^*_2Cr^+$, 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 $Tol_2Cr{\cdot}C_{60}$ 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.

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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: $C_{92}H_{38}Cl_4Cr_1$, black, monoclinic, *C*2/*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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