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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}^{3-} , 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 $Rb^+ \cdot C_{60}^{3-}$ 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}^{3-} radical anions.¹ The absence of any additional bands in the IR spectrum which usually appear with the dimerization or polymerization of fullerenes^{6c} indicates the monomeric state of C_{60}^{3-} at RT.

The RT structure of **1** contains orientationally disordered fullerene molecules but well-ordered $Cp^*_2Cr^+$ units. The C_{60}^{3-} forms the uniform zigzag chains in **1** with the shortest center-to-center distance of about 10.11 Å.

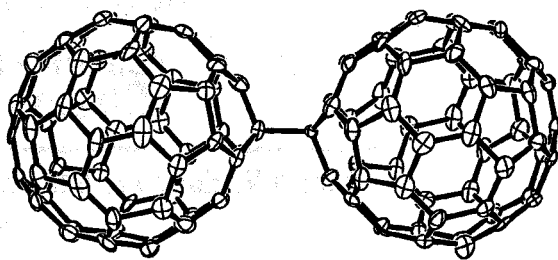


Figure 1. ORTEP drawing of the structure of (C_{60}^-)₂ dimer in **1** at 100 K.

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** was studied at 100 K. In contrast to the RT configuration, the C_{60}^{3-} 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 inter cage 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 inter cage 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 inter cage 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}^{3-} uniform zigzag chains of the RT structure.

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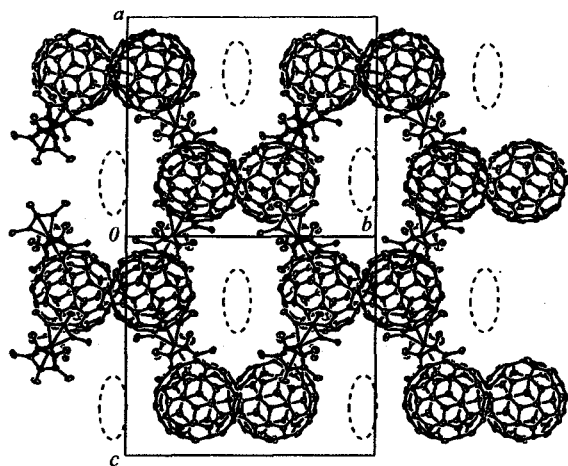


Figure 2. The crystal structure of $\text{Cp}^*_2\text{Cr}\cdot\text{C}_{60}(\text{C}_6\text{H}_4\text{Cl}_2)_2$ (**1**) at 100 K viewed down the [101] direction. The dimers are shown in their major orientation. The dashed ellipses show the channels containing the $\text{C}_6\text{H}_4\text{Cl}_2$ molecules, which are not shown.

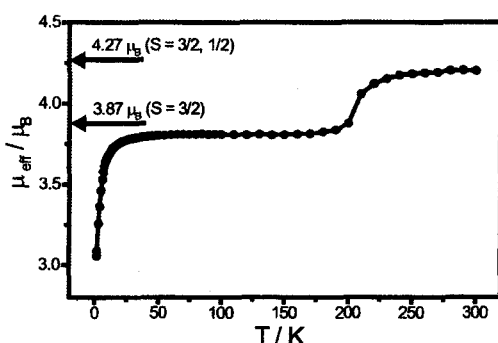


Figure 3. The dependence of the magnetic moment (μ_{eff}) vs temperature for polycrystalline **1** between 300 and 1.9 K. The behavior is reversible.

The magnetic susceptibility of **1** is measured in the 300–1.9 K range (Figure 3). The magnetic moment is equal to $4.20 \mu_{\text{B}}$ at RT. Thus, both spins from Cp^*_2Cr^+ ($S = 3/2$) and $\text{C}_{60}^{\bullet-}$ ($S = 1/2$) contribute to the magnetic susceptibility (the spin-only value expected for a noninteracting $S = 3/2, 1/2$ system is $4.27 \mu_{\text{B}}$). The steplike and reversible change of the magnetic moment of **1** from 4.20 to $3.88 \mu_{\text{B}}$ 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 $3.87 \mu_{\text{B}}$). Thus, the change of the magnetic moment of **1** clearly indicates the disappearance of the contribution of $\text{C}_{60}^{\bullet-}$ spins consistent with the formation of the diamagnetic $(\text{C}_{60}^{\bullet-})_2$ dimers. This situation is similar to that in the ionic $\text{ToI}_2\text{Cr}\cdot\text{C}_{60}$ in which the dimerization of $\text{C}_{60}^{\bullet-}$ at 250 K results in a step decrease of the magnetic moment from 2.5 to $1.72 \mu_{\text{B}}$.^{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 $\text{Cr}^{\text{III}}\text{TPP}^+(\text{C}_{60}^{\bullet-})(\text{THF})_3$ (CrTPP = tetraphenyl-21*H*,23*H*-porphinato chromium, and THF = tetrahydrofuran) which is also EPR-silent^{9a} we can deduce that the interaction of $\text{C}_{60}^{\bullet-}$ 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 $(\text{Cp}^*_2\text{Cr}^+)(\text{PF}_6^-)$ 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 $\text{C}_{60}^{\bullet-}$ occur simultaneously, we can conclude that the formation of diamagnetic $(\text{C}_{60}^{\bullet-})_2$ dimers breakdowns the magnetic coupling between $\text{C}_{60}^{\bullet-}$ and Cp^*_2Cr^+ and leads to the formation of odd-spin EPR-active species containing paramagnetic Cp^*_2Cr^+ and diamagnetic $(\text{C}_{60}^{\bullet-})_2$. A somewhat similar effect has been observed in the ionic $\text{TDAE}^+\cdot\text{C}_{60}^{\bullet-}$ (TDAE = tetrakis(dimethylamino)ethylene) in which the polymerization of $\text{C}_{60}^{\bullet-}$ under pressure (>10 kbar) results in the appearance of the EPR signal from TDAE^+ .^{9b}

In conclusion, a new ionic complex of C_{60} with decamethylchromocene: $\text{Cp}^*_2\text{Cr}\cdot\text{C}_{60}(\text{C}_6\text{H}_4\text{Cl}_2)_2$ (**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 $(\text{C}_{60}^{\bullet-})_2$ 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 $\text{C}_{60}^{\bullet-}$ 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 $4.20 \mu_{\text{B}}$ ($S = 3/2, 1/2$) to $3.88 \mu_{\text{B}}$ ($S = 3/2$), 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 $(\text{C}_{60}^{\bullet-})_2$ dimers. The $(\text{C}_{60}^{\bullet-})_2$ dimers are also formed in similar ionic $\text{ToI}_2\text{Cr}\cdot\text{C}_{60}$ with short distances between the centers of $\text{C}_{60}^{\bullet-}$ (9.97 Å).^{3c} Thus, the $\text{C}_{60}^{\bullet-}$ can dimerize reversibly in the ionic complexes in which the distances between $\text{C}_{60}^{\bullet-}$ 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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- Crystallographic data: (1) 300 K: $\text{C}_{92}\text{H}_{38}\text{Cl}_4\text{Cr}$, black, monoclinic, $C2/c$, $a = 23.167(5)$ Å, $b = 20.983(5)$ Å, $c = 14.609(2)$ Å, $\beta = 123.415(8)^\circ$, $V = 5928(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.498$ g·cm⁻³. (2) 100 K: $\text{C}_{368}\text{H}_{152}\text{Cl}_{16}\text{Cr}_4$, monoclinic, $P2_1$, $a = 22.973(1)$ Å, $b = 20.785(1)$ Å, $c = 24.747(1)$ Å, $\beta = 106.387(3)^\circ$, $V = 11247.7(9)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.579$ g·cm⁻³. $R(F_o) = 0.051$, $wR(F_o^2) = 0.147$, and GOF = 1.013.
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