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Synthesis and Crystal Structure of Ionic Multicomponent Complex: $\{[Cr^{I}(PhH)_2]^{\bullet+}\}_2[Co^{II}TPP(C_{60}(CN)_2)]^{-}$ $[C_{60}(CN)_2]^{\bullet-}\cdot 3(o\text{-}C_6H_4Cl_2)$ Containing $C_{60}(CN)_2^{\bullet-}$ Radical Anion and σ-Bonded Diamagnetic $Co^{II}TPP(C_{60}(CN)_2)^{-}$ Anion

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Electron-transfer salts of fullerene C_{60} are of great interest due to intriguing physical and structural properties.[1] By now the salts of C_{60} have been obtained with tetrakis(dimethylamino)ethylene,[2a] cobaltocene (Cp_2Co^{II}),[2b] bis(benzene)chromium ($Cr^{0}(PhH)_2$),[2c] and some other compounds.[1] The major part of donor molecules (for example tetrachalcogenafulvalenes, porphyrins, and their metal-containing analogues) is cocrystallized with fullerenes, yielding basically neutral complexes.[3] These complexes have various packing motifs of the fullerene molecules in a crystal. In this view one would expect that the design of multicomponent complexes $[D_1(D_2^{+}\cdot\text{fullerene}^{-})]$, where D_1 is a large structure-forming molecule and D_2 is a small molecule with strong donor properties, could be promising for the synthesis of novel ionic compounds of fullerenes with different crystal structures.

$Cr(PhH)_2$ is one of the most suitable donors (D_2) for the synthesis of the ionic complexes[2c] ($E^{+/0}_{1/2}$ of $Cr(PhH)_2 = -0.72$ V *vs* SCE,[4a] calcd -1.12 V *vs* Fc/Fc^{+} (Fc: ferrocene) and $E^{0/-}_{1/2}$ of $C_{60}(CN)_2 = -0.935$ V *vs* Fc/Fc^{+} [4b]). Here we report the synthesis and structural and magnetic properties of the ionic multicomponent complex $\{[Cr^{I}(PhH)_2]^{\bullet+}\}_2[Co^{II}TPP(C_{60}(CN)_2)]^{-}[C_{60}(CN)_2]^{\bullet-}\cdot 3(o\text{-}C_6H_4Cl_2)$ (**1**, $Co^{II}TPP$ = cobalt (II) tetraphenylporphyrin (D_1), $o\text{-}C_6H_4Cl_2$ = *o*-dichlorobenzene). Furthermore, we describe first time the σ-bonding of $Co^{II}TPP$ to dicyanofullerene radical anion, resulting in diamagnetic supramolecular anion $Co^{II}TPP(C_{60}(CN)_2)^{-}$ and the first molecular structure of $C_{60}(CN)_2^{\bullet-}$ radical anion in a crystal.

The crystals of **1** were obtained by the diffusion of hexane into $o\text{-}C_6H_4Cl_2$ solution containing $Co^{II}TPP$, $Cr(PhH)_2$, and $C_{60}(CN)_2$.

The main building block of **1**[5] is $Co^{II}TPP\cdot(C_{60}(CN)_2)_2$ unit (Figure 1). One $C_{60}(CN)_2$ (**A**) in the unit coordinates to $Co^{II}TPP$ by σ-type with the Co···C contact of 2.282(3) Å. This distance is longer than those for the covalent C−Co bond in alkylcobaltoamines (1.99−2.03 Å[6a]) but is essentially shorter than the van der Waals M···C contacts in the neutral complexes of fullerenes with metal-containing porphyrins (2.63−3.32 Å).[3b−e] The shortened Co···C contacts for carbon atoms closest to the σ-bonded carbon are 2.99−3.09 Å. The second $C_{60}(CN)_2$ (**B**) forms only shortened van der Waals contacts with $Co^{II}TPP$ by η^2-type (the Co···C distances of 2.789(3) and 2.928(3) Å). In contrast to the saddlelike shape of the parent $Co^{II}TPP$[6b] the macrocycle is planar in **1** with the Co−N bond distances of 1.967−1.994 Å. The cobalt atom deviates by 0.113(3) Å from the mean plane of the macrocycle toward to the fullerene molecule.

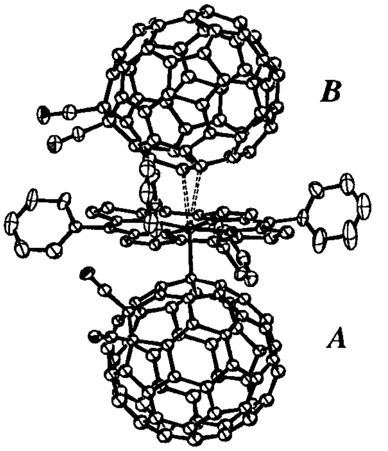

Figure 1. Shortened van der Waals contacts and the σ-bonding of Co^{II}-TPP with $C_{60}(CN)_2^{-}$ (dashed and full lines, respectively).

The 1:1 molar ratio of $Cr(PhH)_2$ and $C_{60}(CN)_2$ in **1** yields the −1 formal charge on the $C_{60}(CN)_2$ molecules. This charged state is in good agreement with the following optical data. The IR bands sensitive to the charge transfer in $Cr(PhH)_2$ shift from 459 and 490 cm^{-1} (the neutral state) to 417 and 460 cm^{-1}, respectively in **1** and coincide with those in $[Cr^{I}(PhH)_2]^{\bullet+}\cdot I^{-}$ (415 and 466 cm^{-1}).[7a]

The most sensitive IR band (the C=C stretching mode) concerning with the charge transfer to $C_{60}(CN)_2$ shifts from 1430 cm^{-1} (the neutral state) to 1391 cm^{-1} in **1** similarly to that of $F_{1u}(4)$ mode of C_{60} which shifts from 1429 cm^{-1} (the neutral state) to 1390−1394 cm^{-1} in $\{(Ph_4X)^{+}\}_2[C_{60}^{\bullet-}]\cdot Y^{-}$ (X = P, As, Y = Cl, I).[7b] The red shift of the C≡N stretching mode from 2241 (the neutral state) to 2230 cm^{-1} in **1** is consistent with the red-shifts in the ionic complexes of tetracyanoquinodimethane (TCNQ)[7c] and in the ionic $[Cp_2Co^{III}]^{+}\cdot[C_{60}(CN)_2]^{\bullet-}CS_2$ (2233 cm^{-1}).[7d] In the UV−vis−NIR spectrum of **1** in the KBr matrix, along with the bands of $Co^{II}TPP$ at 427 and 522 nm and $C_{60}(CN)_2$ at 326 nm, new bands appear in the NIR-range at 1049 nm (9.5×10^{3} cm^{-1}) (the intramolecular transition in $C_{60}(CN)_2^{\bullet-}$, which is observed at 1019 nm in *N*,*N*-dimethylformamide solution[7d]) and at 1205 nm (8.3×10^{3} cm^{-1}). The latter band may be attributed to the charge transfer either in the $Co^{II}TPP(C_{60}(CN)_2)^{-}$ anions or between $C_{60}(CN)_2^{-}$ anions. Accordingly, the ionic formula of **1** is deduced to be $\{[Cr^{I}(PhH)_2]^{\bullet+}\}_2[Co^{II}TPP(C_{60}(CN)_2)]^{-}[C_{60}(CN)_2]^{\bullet-}\cdot 3(o\text{-}C_6H_4Cl_2)$.

Compound **1** is a unique example of the cage structure with large channels accommodating $Cr^{I}(PhH)_2^{\bullet+}$ and $o\text{-}C_6H_4Cl_2$ molecules. Two types of channels with different sizes are formed along the *a*-axis (Figure 2). The channel I is occupied by the ordered $Cr^{I}(PhH)_2^{\bullet+}$ surrounded by six $C_{60}(CN)_2^{-}$ among which four molecules (2***A*** + 2***B***) project negatively charged C≡N groups to the central $Cr^{I}(PhH)_2^{\bullet+}$, forming several $N\cdots C(Cr^{I}(PhH)_2^{\bullet+})$ contacts in 3.24−3.26 Å range and two other $C_{60}(CN)_2^{\bullet-}$ (2***B***) to the $Cr^{I}(PhH)_2^{\bullet+}$ embedded in the neighboring channels I. The channel

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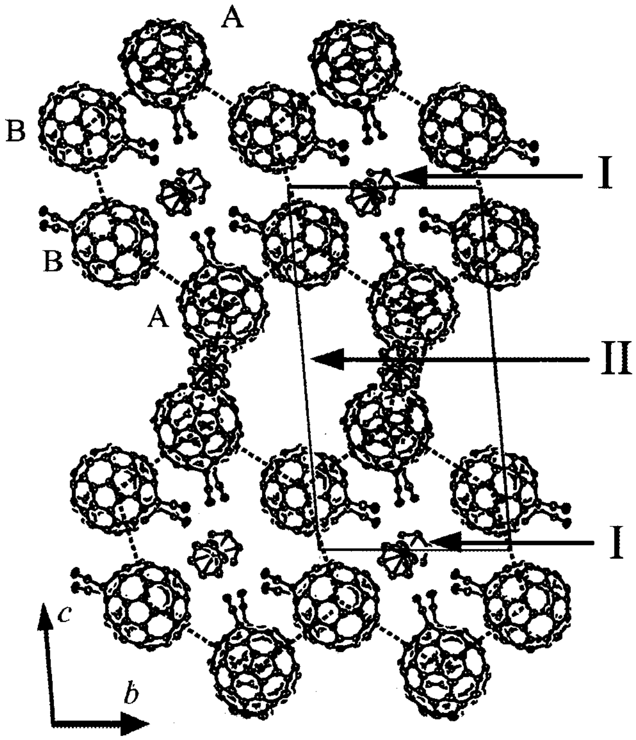

Figure 2. View of the packing of $C_{60}(CN)_2^-$ and $Cr^I(PhH)_2^{\bullet+}$ along the *a*-axis. The $Co^{II}TPP$, $o\text{-}C_6H_4Cl_2$ molecules and the disordered $Cr^I(PhH)_2^{\bullet+}$ are omitted. The honeycomb network is shown by dotted lines.

II has the larger size than I because its walls are composed of six $C_{60}(CN)_2^-$ (4***A*** + 2***B***) and the additional ordered $Cr^I(PhH)_2^{\bullet+}$. The channel II contains the disordered $Cr^I(PhH)_2^{\bullet+}$ and $o\text{-}C_6H_4Cl_2$ (not depicted in Figure 2) in two crystallographically independent positions, one of which is occupied by $o\text{-}C_6H_4Cl_2$ only and another is shared by both $Cr^I(PhH)_2^{\bullet+}$ and $o\text{-}C_6H_4Cl_2$ with the occupancy factor of 0.50 and 0.35, respectively. The fullerenes have several shortened contacts to one another (3.17−3.38 Å).

The nonbonded $C_{60}(CN)_2^{\bullet-}$ (***B***) retains both the C_{2v} symmetry and the shape of the molecule. The average bond angle for the sp^3 carbons of 109° is close to the tetrahedral geometry. The lengths of the 6−6 and 6−5 bonds (except bonds with sp^3 carbons) are averaged to 1.392(12) and 1.449(12) Å, respectively, and are close to those for the neutral molecule.[4b] The retention of $C_{60}(CN)_2^{\bullet-}$ molecular shape may be attributed to the nondegenerate LUMO orbital[7d] and the absence of Jahn−Teller effect. The length of the C≡N bonds are 1.141(6) and 1.152(6) Å.

The magnetic susceptibility of **1** at room temperature ($\mu_{eff} = 2.91\ \mu_B$) is most likely defined by three noninteracting 1/2-spins per formula unit (μ_{eff} of 3.00 μ_B) rather than by two (μ_{eff} of 2.45 μ_B). The EPR signal has $g = 1.991$ with line width of $\Delta H =$ 11 mT at room temperature and strongly narrows with the temperature decrease ($\Delta H = 2.6$ mT at 200 K). Below 180 K the signal splits into two components with $g_1 = 1.996$ and $g_2 = 1.988$ with $\Delta H = 1.6$ and 1.9 mT, respectively. After the splitting, the *g*-factors and line width of the components only weakly depend on temperature down to 4 K. The two components may be attributed to two different signals from $Cr^I(PhH)_2^{\bullet+}$ [8] (g_2) and the resonating one (g_1) between $C_{60}(CN)_2^{\bullet-}$ and $Cr^I(PhH)_2^{\bullet+}$. The latter signal is characteristic of a strong exchange coupling and has the mean *g*-factor between those for $C_{60}(CN)_2^{\bullet-}$ ($g = 1.9998$)[7d] and $Cr^I(PhH)_2^{\bullet+}$ ($g = 1.9860$).[8] Thus, according to the EPR data the spins come from the $Cr^I(PhH)_2^{\bullet+}$ (two-spin, $S = {}^1/_2$) and the nonbonded $C_{60}(CN)_2^{\bullet-}$ (***B***, one spin, $S = {}^1/_2$). Consequently, the $CoTPP(C_{60}(CN)_2)^-$ anions are deduced to be diamagnetic. It should be noted that the covalently bonded $Co^{II}TPP{\bullet}NO$ compound with similar electronic configuration (Co(II) (d^7), NO (π^{*1})) is also diamagnetic and EPR silent.[9]

The complex **1** is a paramagnet with a negative Weiss constant ($\Theta = -2.4$ K). This is attributed to the magnetic dilution of the paramagnetic $Cr^I(PhH)_2^{\bullet+}$ and the nonbonded $C_{60}(CN)_2^{\bullet-}$ by the diamagnetic $Co^{II}TPP(C_{60}(CN)_2)^-$ units. The complex has room-temperature conductivity of 4×10^{-5} S•cm^{-1} which is characteristic of fullerene-containing salts with bulky cations.[1c]

Thus, the synthesis of the multicomponent complex **1** allows us to study for the first time the interaction of $Co^{II}TPP$ with fullerene radical anions. The most characteristic features of the title complex are: (1) the σ-bonding between Co and one of two $C_{60}(CN)_2^{\bullet-}$ (Figure 1), (2) the ionic ground state of $\{[Cr^I(PhH)_2]^{\bullet+}\}_2[Co^{II}TPP\text{-}(C_{60}(CN)_2)]^-[C_{60}(CN)_2]^{\bullet-}{\bullet}3(o\text{-}C_6H_4Cl_2)$, and (3) the cage structure built by the stack of the honeycomb network (Figure 2) with channels accommodating $Cr^I(PhH)_2^{\bullet+}$ and $o\text{-}C_6H_4Cl_2$ molecules. The σ-bonding is likely formed due to the presence of an additional electron on the π^*-level of $C_{60}(CN)_2^{\bullet-}$ radical anion which interacts with $d_z{}^2$-orbital of $Co^{II}TPP$. As a result the unusual diamagnetic $Co^{II}TPP(C_{60}(CN)_2)^-$ anions are formed. On the whole, this work shows that $C_{60}(CN)_2^{\bullet-}$ is able to form the essentially shorter M•••C contacts with metal-containing porphyrins than the neutral fullerenes.

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

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(5) Crystallographic data for **1**: $C_{420}H_{128}N_{16}Cl_{12}Co_2Cr_4$, triclinic, space group $P\bar{1}$, $a = 13.967(1)$ Å, $b = 15.928(1)$ Å, $c = 30.332(2)$ Å, $\alpha = 92.30(1)°$, $\beta = 100.89(1)°$, $\gamma = 103.46(1)°$, $V = 6419.3(6)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.591$ g cm^{-3}. T = 120 K. $R(F_o) = 0.084$, $wR\ (F_o{}^2) = 0.188$, GOF = 1.024.

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