

Synthesis and Crystal Structure of Ionic Multicomponent Complex: $\{[\text{Cr}^{\text{I}}(\text{PhH})_2]^{+}\}_2[\text{Co}^{\text{II}}\text{TPP}(\text{C}_{60}(\text{CN})_2)]^{-}[\text{C}_{60}(\text{CN})_2]^{-}\cdot 3(o\text{-C}_6\text{H}_4\text{Cl}_2)$ Containing $\text{C}_{60}(\text{CN})_2^{-}$ Radical Anion and σ -Bonded Diamagnetic $\text{Co}^{\text{II}}\text{TPP}(\text{C}_{60}(\text{CN})_2)^{-}$ Anion

Dmitry V. Konarev,^{*†} Salavat S. Khasanov,[‡] Akihiro Otsuka, Yukihiro Yoshida, and Gunzi Saito^{*}

Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

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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 ($\text{Cp}_2\text{Co}^{\text{II}}$),^{2b} bis(benzene)chromium ($\text{Cr}^0(\text{PhH})_2$),^{2c} and some other compounds.¹ The major part of donor molecules (for example tetrachalcogenafullerenes, 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 $[\text{D}_1(\text{D}_2^{+}\text{-fullerene}^{-})]$, 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.

$\text{Cr}(\text{PhH})_2$ is one of the most suitable donors (D_2) for the synthesis of the ionic complexes^{2c} ($E^{+/0}_{1/2}$ of $\text{Cr}(\text{PhH})_2 = -0.72$ V *vs* SCE,^{4a} calcd -1.12 V *vs* Fc/Fc^{+} (Fc : ferrocene) and $E^{0/-}_{1/2}$ of $\text{C}_{60}(\text{CN})_2 = -0.935$ V *vs* Fc/Fc^{+} ^{4b}). Here we report the synthesis and structural and magnetic properties of the ionic multicomponent complex $\{[\text{Cr}^{\text{I}}(\text{PhH})_2]^{+}\}_2[\text{Co}^{\text{II}}\text{TPP}(\text{C}_{60}(\text{CN})_2)]^{-}[\text{C}_{60}(\text{CN})_2]^{-}\cdot 3(o\text{-C}_6\text{H}_4\text{Cl}_2)$ (**1**, $\text{Co}^{\text{II}}\text{TPP}$ = cobalt (II) tetraphenylporphyrin (D_{4h}), $o\text{-C}_6\text{H}_4\text{Cl}_2$ = *o*-dichlorobenzene). Furthermore, we describe first time the σ -bonding of $\text{Co}^{\text{II}}\text{TPP}$ to dicyanofullerene radical anion, resulting in diamagnetic supramolecular anion $\text{Co}^{\text{II}}\text{TPP}(\text{C}_{60}(\text{CN})_2)^{-}$ and the first molecular structure of $\text{C}_{60}(\text{CN})_2^{-}$ radical anion in a crystal.

The crystals of **1** were obtained by the diffusion of hexane into $o\text{-C}_6\text{H}_4\text{Cl}_2$ solution containing $\text{Co}^{\text{II}}\text{TPP}$, $\text{Cr}(\text{PhH})_2$, and $\text{C}_{60}(\text{CN})_2$.

The main building block of **1**⁵ is $\text{Co}^{\text{II}}\text{TPP}(\text{C}_{60}(\text{CN})_2)_2$ unit (Figure 1). One $\text{C}_{60}(\text{CN})_2$ (**A**) in the unit coordinates to $\text{Co}^{\text{II}}\text{TPP}$ by σ -type with the $\text{Co}\cdots\text{C}$ 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 $\text{M}\cdots\text{C}$ contacts in the neutral complexes of fullerenes with metal-containing porphyrins (2.63–3.32 Å).^{3b–c} The shortened $\text{Co}\cdots\text{C}$ contacts for carbon atoms closest to the σ -bonded carbon are 2.99–3.09 Å. The second $\text{C}_{60}(\text{CN})_2$ (**B**) forms only shortened van der Waals contacts with $\text{Co}^{\text{II}}\text{TPP}$ by η^2 -type (the $\text{Co}\cdots\text{C}$ distances of 2.789(3) and 2.928(3) Å). In contrast to the saddlelike shape of the parent $\text{Co}^{\text{II}}\text{TPP}$ ^{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.

The 1:1 molar ratio of $\text{Cr}(\text{PhH})_2$ and $\text{C}_{60}(\text{CN})_2$ in **1** yields the -1 formal charge on the $\text{C}_{60}(\text{CN})_2$ molecules. This charged state

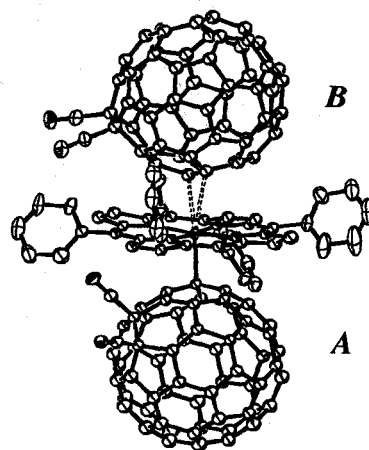


Figure 1. Shortened van der Waals contacts and the σ -bonding of $\text{Co}^{\text{II}}\text{TPP}$ with $\text{C}_{60}(\text{CN})_2^{-}$ (dashed and full lines, respectively).

is in good agreement with the following optical data. The IR bands sensitive to the charge transfer in $\text{Cr}(\text{PhH})_2$ shift from 459 and 490 cm^{-1} (the neutral state) to 417 and 460 cm^{-1} , respectively in **1** and coincide with those in $[\text{Cr}^{\text{I}}(\text{PhH})_2]^{+}\text{I}^{-}$ (415 and 466 cm^{-1}).^{7a}

The most sensitive IR band (the C=C stretching mode) concerning with the charge transfer to $\text{C}_{60}(\text{CN})_2$ 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 $\{(\text{Ph}_4\text{X})^{+}\}_2[\text{C}_{60}^{2-}]\cdot\text{Y}^{-}$ ($\text{X} = \text{P}, \text{As}, \text{Y} = \text{Cl}, \text{I}$).^{7b} The red shift of the $\text{C}\equiv\text{N}$ 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 $[\text{Cp}_2\text{Co}^{\text{III}}]^{+}[\text{C}_{60}(\text{CN})_2]^{-}\text{CS}_2$ (2233 cm^{-1}).^{7d} In the UV–vis–NIR spectrum of **1** in the KBr matrix, along with the bands of $\text{Co}^{\text{II}}\text{TPP}$ at 427 and 522 nm and $\text{C}_{60}(\text{CN})_2$ at 326 nm, new bands appear in the NIR-range at 1049 nm (9.5×10^3 cm^{-1}) (the intramolecular transition in $\text{C}_{60}(\text{CN})_2^{-}$, 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 $\text{Co}^{\text{II}}\text{TPP}(\text{C}_{60}(\text{CN})_2)^{-}$ anions or between $\text{C}_{60}(\text{CN})_2^{-}$ anions. Accordingly, the ionic formula of **1** is deduced to be $\{[\text{Cr}^{\text{I}}(\text{PhH})_2]^{+}\}_2[\text{Co}^{\text{II}}\text{TPP}(\text{C}_{60}(\text{CN})_2)]^{-}[\text{C}_{60}(\text{CN})_2]^{-}\cdot 3(o\text{-C}_6\text{H}_4\text{Cl}_2)$.

Compound **1** is a unique example of the cage structure with large channels accommodating $\text{Cr}^{\text{I}}(\text{PhH})_2^{+}$ and $o\text{-C}_6\text{H}_4\text{Cl}_2$ molecules. Two types of channels with different sizes are formed along the *a*-axis (Figure 2). The channel I is occupied by the ordered $\text{Cr}^{\text{I}}(\text{PhH})_2^{+}$ surrounded by six $\text{C}_{60}(\text{CN})_2^{-}$ among which four molecules (**2A** + **2B**) project negatively charged $\text{C}\equiv\text{N}$ groups to the central $\text{Cr}^{\text{I}}(\text{PhH})_2^{+}$, forming several $\text{N}\cdots\text{C}(\text{Cr}^{\text{I}}(\text{PhH})_2^{+})$ contacts in 3.24–3.26 Å range and two other $\text{C}_{60}(\text{CN})_2^{-}$ (**2B**) to the $\text{Cr}^{\text{I}}(\text{PhH})_2^{+}$ embedded in the neighboring channels I. The channel

^{*} Corresponding authors. E-mail: (D.V.K.) konarev@icp.ac.ru and (G.S.) saito@kuchem.kyoto-u.ac.jp.

[†] On leave from Institute of Problems of Chemical Physics RAS, Chernogolovka, Moscow region 142432, Russia.

[‡] On leave from Institute of Solid State Physics RAS, Chernogolovka, Moscow region, 142432, Russia.

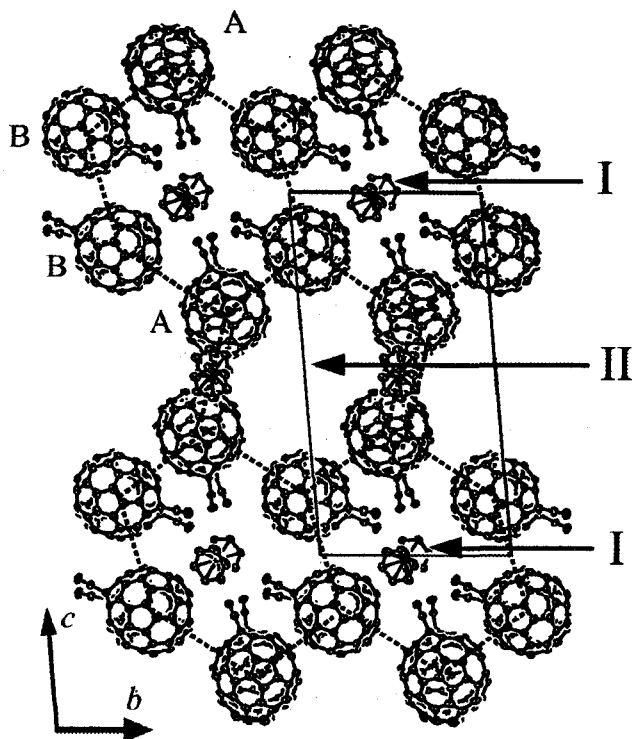


Figure 2. View of the packing of $C_{60}(CN)_2^-$ and $CrI(PhH)_2^{+}$ along the a -axis. The $Co^{II}TPP$, o - $C_6H_4Cl_2$ molecules and the disordered $CrI(PhH)_2^{+}$ are omitted. The honeycomb network is shown by dotted lines.

II has the larger size than I because its walls are composed of six $C_{60}(CN)_2^-$ ($4A + 2B$) and the additional ordered $CrI(PhH)_2^{+}$. The channel II contains the disordered $CrI(PhH)_2^{+}$ and o - $C_6H_4Cl_2$ (not depicted in Figure 2) in two crystallographically independent positions, one of which is occupied by o - $C_6H_4Cl_2$ only and another is shared by both $CrI(PhH)_2^{+}$ and o - $C_6H_4Cl_2$ 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 $C_{60}(CN)_2^-$ (**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 $C_{60}(CN)_2^-$ molecular shape may be attributed to the nondegenerate LUMO orbital^{7d} and the absence of Jahn–Teller effect. The length of the $C\equiv N$ 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 $3.00 \mu_B$) rather than by two (μ_{eff} of $2.45 \mu_B$). 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 $CrI(PhH)_2^{+}$ (g_2) and the resonating one (g_1) between $C_{60}(CN)_2^-$ and $CrI(PhH)_2^{+}$. The latter signal is characteristic of a strong exchange coupling and has the mean g -factor between those for $C_{60}(CN)_2^-$ ($g = 1.9998$)^{7d} and $CrI(PhH)_2^{+}$ ($g = 1.9860$).⁸ Thus, according to the EPR data the spins come from the $CrI(PhH)_2^{+}$ (two-spin, $S = 1/2$) and the nonbonded $C_{60}(CN)_2^-$ (**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 $Co^{II}TPP\cdot NO$ 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 $CrI(PhH)_2^{+}$ and the nonbonded $C_{60}(CN)_2^-$ by the diamagnetic $Co^{II}TPP(C_{60}(CN)_2)^-$ units. The complex has room-temperature conductivity of $4 \times 10^{-5} S \cdot cm^{-1}$ 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 $C_{60}(CN)_2^-$ (Figure 1), (2) the ionic ground state of $\{[CrI(PhH)_2^{+}]_2[Co^{II}TPP(C_{60}(CN)_2)]^-[C_{60}(CN)_2]^{*-} \cdot 3(o-C_6H_4Cl_2)]$, and (3) the cage structure built by the stack of the honeycomb network (Figure 2) with channels accommodating $CrI(PhH)_2^{+}$ and o - $C_6H_4Cl_2$ molecules. The σ -bonding is likely formed due to the presence of an additional electron on the π^* -level of $C_{60}(CN)_2^-$ radical anion which interacts with d^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 $C_{60}(CN)_2^-$ is able to form the essentially shorter $M \cdots C$ 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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- Crystallographic data for **1**: $C_{42}H_{128}N_{16}Cl_{12}Co_2Cr_4$, triclinic, space group $P1$, $a = 13.967(1)$ Å, $b = 15.928(1)$ Å, $c = 30.332(2)$ Å, $\alpha = 92.30(1)^\circ$, $\beta = 100.89(1)^\circ$, $\gamma = 103.46(1)^\circ$, $V = 6419.3(6)$ Å³, $Z = 1$, $\rho_{calcd} = 1.591$ g cm⁻³, $T = 120$ K, $R(F_o) = 0.084$, $wR(F_o^2) = 0.188$, $GOF = 1.024$.
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