Multicomponent Ionic Complexes of Cobalt(II) Tetraphenylporphyrin with C_{60} Fullerides − Transition from the σ-Bonded [(Co^{II}TPP)·(C_{60}^{-})] Anion to Nonbonded Co^{II}TPP and $C_{60}^{\cdot -}$ Components

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New multicomponent ionic complexes containing [(Cation$^+$)·(C_{60}^{-})] fullerides and neutral Co^{II}TPP molecules were obtained [the cations are Cs$^+$ (**1**), tetramethylammonium $(CH_3)_4N^+$ (**2**) and *N*-methylpyridinium *N*-MePy$^+$ (**3**)]. The crystal structure of **1** determined from single-crystal X-ray diffraction analysis contains chains of alternating Co^{II}TPP and $C_{60}^{\cdot -}$ units with voids accommodating solvated [(Cs$^+$)·$(C_6H_5CN)_{1.64}$]·CH_3CN counter cations. Relatively long Co···C distances between Co^{II}TPP and $C_{60}^{\cdot -}$ in **1** (2.55–3.05 Å) indicate the absence of noticeable bonding of Co^{II}TPP and $C_{60}^{\cdot -}$. This is consistent with the EPR spectrum of **1**, which manifests two EPR signals with $g = 2.0009$ and 2.4982 attributable to $C_{60}^{\cdot -}$ and Co^{II}TPP, respectively. In contrast to **1**, complexes **2** and **3** contain EPR-silent, σ-bonded [(Co^{II}TPP)·(C_{60}^{-})] anions. The influence of the size of counter cations on the stability of σ-bonded [(Co^{II}TPP)·(C_{60}^{-})] anions in ionic [(Cation$^+$)·(Co^{II}TPP)·(C_{60}^{-})] complexes is analyzed.

Introduction

Fullerene C_{60}-based compounds possess unique magnetic, conductive, and photoactive properties.[1,2] From this variety of compounds, fullerene assemblies with metal-containing porphyrins are of special interest due to possible applications in energy transducers and the modeling of artificial photosynthesis.[2,3] About several tens of fullerene donor−acceptor complexes ranging from molecular to ionic ones,[4−9] as well as covalently and noncovalently linked dyads and triads[3] were obtained with metal octaethyl- and tetraphenylporphyrins. In this context it is very important to understand the metal−fullerene interaction that occurs in such assemblies. Neutral fullerenes are considered to be relatively weak ligands when they coordinate with metal-containing porphyrins.[8,9] Among different metalloporphyrins only iron(II), iron(III), and cobalt(II) tetraphenylporphyrins form short M···C(C_{60}) contacts of 2.58−2.63, 2.57, and 2.58−2.69 Å, respectively, with C_{60}.[10−13] These contacts are shorter than the sum of the van der Waals radii of the M and C atoms, but essentially longer than typical M···C distances when a strong M···C bond is formed, for example, in alkylcobalamins (1.99−2.03 Å).[14]

The preparation of the multicomponent ionic complexes [{Cr^I$(C_6H_6)_2^{\cdot +}$}·(Co^{II}TPP·fullerene$^-$)·$(C_6H_4Cl_2)$] allows us to study the interaction of cobalt(II) tetraphenylporphyrin with fullerene radical anions of C_{60}, C_{70}, and $C_{60}CN_2$. It turned out that the fullerene radical anions are bound more strongly to Co^{II}TPP than neutral fullerenes and form unusual diamagnetic σ-bonded (Co^{II}TPP·fullerene$^-$) anions with shortened Co···C(fullerene$^-$) distances of 2.28−2.32 Å.[13,15] However, these interatomic distances are longer than those for the strong M···C bond in alkylcobalamins and indicate a relatively weak σ-bond in (Co^{II}TPP·fullerene$^-$) anions. Therefore, the dissociation of these anions could be expected. Indeed, the study of another multicomponent ionic complex with bulkier tetrakis(dimethylamino)ethylene — [(TDAE$^{\cdot +}$)·(Co^{II}TPP·$C_{60}^{\cdot -}$)] — indicates the presence of diamagnetic σ-bonded [Co^{II}TPP·C_{60}^{-}] anions in the 2−190 K range, which dis-

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sociate to paramagnetic and EPR-active, nonbonded Co^{II}-TPP and $C_{60}^{\cdot -}$ components at temperatures higher than 190 K.[16]

Here we report on new multicomponent ionic complexes containing $[Cation^{+}\cdot C_{60}^{-}]$ fullerides and neutral $Co^{II}TPP$, where the cations are Cs^{+} (in **1**), tetramethylammonium $(CH_3)_4N^{+}$ (in **2**), and *N*-methylpyridinium *N*-$MePy^{+}$ (in **3**). The crystal structure of $[(Cs^{+})\cdot(Co^{II}TPP)\cdot(C_{60}^{\cdot -})\cdot(C_6H_5CN)_{1.64}\cdot(C_6H_4Cl_2)_{0.36}\cdot CH_3CN]$ (**1**), the IR and EPR spectra of **1**, $[\{(CH_3)_4N^{+}\}\cdot(Co^{II}TPP\cdot C_{60}^{-})\cdot(C_6H_5CN)\cdot(C_6H_4Cl_2)]$ (**2**), and $[(N\text{-}MePy^{+})\cdot(Co^{II}TPP\cdot C_{60}^{-})\cdot(C_6H_4Cl_2)_{1.2}]$ (**3**) are presented. For the first time, the complex containing nonbonded $Co^{II}TPP$ and $C_{60}^{\cdot -}$ components in the 4−290 K range is described and its properties are compared with those of the complexes containing diamagnetic σ-bonded $[Co^{II}TPP\cdot C_{60}^{-}]$ anions.

Results and Discussion

The resulting complexes are presented in Table 1. Crystals of **1−3** were obtained by diffusion of *n*-hexane into a solution containing the corresponding $[Cation^{+}\cdot C_{60}^{\cdot -}]$ salts and $Co^{II}TPP$ in anaerobic conditions. The crystal structure of **1** was studied at 110 K.[17] Two crystallographically independent $Co^{II}TPP$ molecules are located in inversion centers, whereas $C_{60}^{\cdot -}$, Cs^{+}, and the solvent C_6H_5CN, $C_6H_4Cl_2$, and CH_3CN molecules are in general positions. The $C_{60}^{\cdot -}$ units are disordered between two orientations (40:60 occupancy) related to each other by their rotation about the noncrystallographic fourfold axis passing through the molecular centroid and the midpoints of two 6−6 bonds.

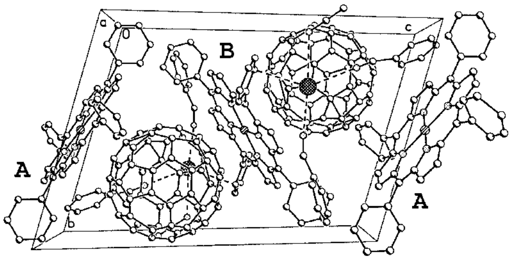

Figure 1. The crystal structure of **1**; the disordered $C_6H_4Cl_2$ molecules are omitted; only the major orientation of $C_{60}^{\cdot -}$ is shown

The main structural motif of the complex is a zigzag chain of alternating $Co^{II}TPP$ and $C_{60}^{\cdot -}$ molecules (Figure 1). Similar motifs were found in the neutral complexes of fullerenes with both metal-containing and metal-free tetraphenylporphyrins.[5−7,13] Each C_{60} unit forms shortened contacts with two $Co^{II}TPP$ molecules (Figure 1). The shortest $Co\cdots C(C_{60})$ contacts are in the 2.55−3.07 Å range for both orientations of C_{60}. These contacts are of the σ-type (Figure 2); however, they are longer than those in the σ-bonded diamagnetic $[Co^{II}TPP\cdot fullerene^{-}]$ anions (fullerene: C_{60} and $C_{60}CN_2$; 2.28−2.32 Å)[13,15] and close to those in the neutral complexes of Fe^{II}, Fe^{III}, and $Co^{II}TPP$ with C_{60} (2.57−2.69 Å)[10−13]. Thus, in contrast to the previously studied ionic complexes $[\{Cr^{I}(C_6H_6)_2^{\cdot +}\}_{1.7}\cdot\{(Co^{II}TPP\cdot C_{60})_2\}^{1.7-}\cdot(C_6H_4Cl_2)_{3.3}]$ and $[(TDAE^{\cdot +})\cdot(Co^{II}TPP\cdot C_{60}^{-})]$, **1** contains nonbonded $Co^{II}TPP$ and $C_{60}^{\cdot -}$ components at 110 K. The weakness of the $Co\cdots C_{60}^{\cdot -}$ bonding in **1** is also justified by the rotation disorder of the $C_{60}^{\cdot -}$ radical anions, whereas they are ordered in the complex $[\{Cr^{I}(C_6H_6)_2^{\cdot +}\}_{1.7}\cdot\{(Co^{II}TPP\cdot C_{60})_2\}^{1.7-}\cdot(C_6H_4Cl_2)_{3.3}]$.[13] A dihedral angle of 63.8° between the planes of the porphyrin macrocycles of **A** and **B** (Figure 1) is larger in **1** than those in the neutral complexes of tetraphenylporphyrins with fullerenes: 39.0° in $[Cu^{II}TPP\cdot C_{70}\cdot(C_6H_5Me)_{1.5}\cdot(Cl_2C{=}CHCl)_{0.5}]$;[6] 44.1° in $[Co^{II}TPP\cdot C_{60}\cdot(C_6H_4Cl_2)_{2.5}]$,[13] and 45.3° in $[H_2TPP\cdot C_{60}\cdot(C_6H_5Me)_3]$.[5]

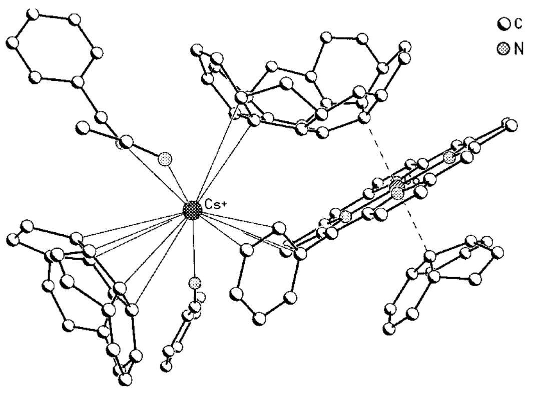

Figure 2. Coordination surrounding of the Cs^{+} cation and the cobalt atom of $Co^{II}TPP$ in the crystal structure of **1**; the disordered $C_6H_4Cl_2$ molecules are omitted; only the major orientation of $C_{60}^{\cdot -}$ is shown

Table 1. The data for crystals of **1−3**

No.	Complex	Elemental analysis found/calcd. C H, N, Cl, Difference (%)[a]					Shape
1	$Cs\cdot Co^{II}TPP\cdot C_{60}\cdot(C_6H_5CN)_{1.64}(C_6H_4Cl_2)_{0.36}\cdot CH_3CN$	According to X-ray diffraction data					prisms
2	$\{(CH_3)_4N\}\cdot(Co^{II}TPP\cdot C_{60})\cdot(C_6H_5CN)\cdot(C_6H_4Cl_2)$	81.36/ 82.30	3.02/ 2.94	4.66/ 5.04	3.67/ 4.26	7.29/ 3.54 (Co), 1.92 (O)	prisms
3	*N*-$MePy\cdot Co^{II}TPP\cdot C_{60}\cdot(C_6H_4Cl_2)_{1.2}$	81.14/ 82.98	2.72/ 2.42	4.12/ 4.15	4.99/ 5.05	7.03/ 3.50 (Co), 1.90 (O)	prisms

[a] The difference (100 %) − (C, H, N, Cl %).

Cesium cations occupy the voids in the $Co^{II}TPP$ and $C_{60}^{\cdot-}$ packing and have an irregular environment. The coordination sphere of Cs^+ (Figure 2) involves nitrogen atoms of one CH_3CN and two disordered C_6H_5CN molecules, six carbon atoms from a hexagonal facet of one $C_{60}^{\cdot-}$ in one orientation or five carbon atoms from a pentagonal facet in the other orientation, two carbon atoms of a 6−6 bond of another closest $C_{60}^{\cdot-}$ (in both orientations), and four carbon atoms from phenyl substituents of $Co^{II}TPP$. The total number of carbon and nitrogen atoms coordinated to Cs^+ is 15; the Cs···N distances are in the 3.05−3.21 Å range and the Cs···C distances in the 3.43−3.86 Å range. However, the $(Cs^+)\cdots(C_{60}^{\cdot-})$ interaction is unable to lower the rotational disorder of $C_{60}^{\cdot-}$. In other Cs^+-containing compounds (according to the Cambridge Structural Database) the coordination number of Cs varies between 14−19, the Cs···N distances are in the range 3.07−3.30 Å, and the Cs···C distances are in the range 3.44−3.69 Å. Cesium fulleride Cs_6C_{60}[18] provides an example of a carbon-only coordination sphere of Cs that contains 22 atoms with $Cs\cdots C(C_{60})$ distances of 3.37−3.69 Å.

Fullerene radical anions are located in pairs isolated from one another by the $Co^{II}TPP$ molecules and the $[(Cs^+)\cdot(C_6H_5CN)_{1.64}\cdot(C_6H_4Cl_2)_{0.36}\cdot CH_3CN]$ aggregates. A center-to-center distance between two $C_{60}^{\cdot-}$ radical anions in the pair is 9.88 Å and the interfullerene C···C distances are in the range 3.07−3.48 Å. The intercenter and the interfullerene C···C contacts in the pair of $C_{60}^{\cdot-}$ are slightly shorter than those in van der Waals neutral complexes of C_{60}.[19] It is quite unusual that in spite of the rather short C···C contacts between $C_{60}^{\cdot-}$, they are not dimerized at temperatures as low as 110 K, whereas in various ionic complexes of C_{60} with metallocenes, such dimerization is observed even at 160−250 K.[20]

The porphyrin macrocycle of $Co^{II}TPP$ retains its planar shape (the root-mean-square deviation of atoms from the mean plane in the porphyrin macrocycle is only 0.017 and 0.015 Å for molecules **A** and **B** in Figure 1, respectively). Such conformation is characteristic of most of the metal-containing tetraphenylporphyrins in the complexes with C_{60}.[5−7,13] The cobalt atom of $Co^{II}TPP$ does not deviate from the mean plane of the porphyrin macrocycle towards the fullerene indicating the absence of noticeable $Co\cdots C(C_{60}^{\cdot-})$ bonding in **1**. On the contrary, these deviations are essentially larger (0.091−0.113 Å) in $[\{Cr^I(C_6H_6)_2^{\cdot+}\}\cdot(Co^{II}TPP\cdot fullerene^-)\cdot C_6H_4Cl_2]$ (fullerene: C_{60} and $C_{60}CN_2$).[13,15]

Thus, complex **1** differs from the previously studied multicomponent ionic complexes of $Co^{II}TPP$ with C_{60}^- by the presence of nonbonded $Co^{II}TPP$ and $C_{60}^{\cdot-}$ components. The IR and EPR spectra of **1** support this assertion.

The IR spectrum of **1** is a superposition of the spectra of neutral $Co^{II}TPP$, $C_{60}^{\cdot-}$, and solvent molecules.[21] The position of the $F_{1u}(4)$ C_{60} mode at 1397 cm^{-1} coincides with those for other radical anion salts of C_{60} with a −1 charge on the C_{60} molecule.[22,23] The integral intensity of the $F_{1u}(2)$ mode at 576 cm^{-1} is also essentially higher than that of the $F_{1u}(1)$ mode at 526 cm^{-1}. The bands attributable to "silent" modes of C_{60} are not observed in the spectrum of **1**[21] indicating the retention of $C_{60}^{\cdot-}$ symmetry and the absence of noticeable σ-bonding between $Co^{II}TPP$ and $C_{60}^{\cdot-}$ at room temperature (*RT* = 290 K). On the contrary, the formation of σ-bonded $(Co^{II}TPP\cdot C_{60}^-)$ anions in $[\{Cr^I(C_6H_6)_2^{\cdot+}\}_{1.7}\cdot\{(Co^{II}TPP\cdot C_{60})_2\}^{1.7-}\cdot(C_6H_4Cl_2)_{3.3}]$ results in the appearance of weak additional bands due to C_{60} symmetry breaking.[13]

The EPR spectrum of **1** contains two intense EPR signals with $g = 2.0009$ [Figure 3 (a)] and 2.4982 [(Figure 3 (b)] and the line halfwidth (ΔH) of 4.78 and 51.2 mT, respectively. The total integrated intensity of these signals corresponds to approximately two spins per one formula unit. On the contrary, the σ-bonded $(Co^{II}TPP\cdot C_{60}^-)$ anions are diamagnetic and EPR silent.[13,15,16] The first signal in **1** is unambiguously attributed to the nonbonded $C_{60}^{\cdot-}$ radical anions. The line halfwidth of this signal monotonically decreases down to 0.3 mT at 4 K. Such behavior is also characteristic of the EPR signal from $C_{60}^{\cdot-}$. The second signal can be attributed to $Co^{II}TPP$ with $S = 1/2$ ground state. This signal is essentially different from that of the parent porphyrin $Co^{II}TPP$ (the asymmetric signal with $g_\perp = 3.322$ and $g_{//} = 1.798$)[24] and similar to the EPR signals from $Co^{II}TPP$ in the neutral complexes with fullerenes C_{60}, C_{70}, and $C_{60}CN_2$ (the asymmetric signals with $g_\perp = 2.51-2.64$ and $\Delta H = 15-30$ mT, $g_{//} = 2.28-2.42$ and $\Delta H = 31-45$ mT).[13] The difference implies that the EPR signal in **1** is a symmetric Lorentzian line down to 4 K, whereas the EPR signals in the neutral complexes with fullerenes are asymmetric and contain two components down to 4 K. The *g*-factor of the EPR signal of $Co^{II}TPP$ in **1** shifts to smaller values as the temperature decreases

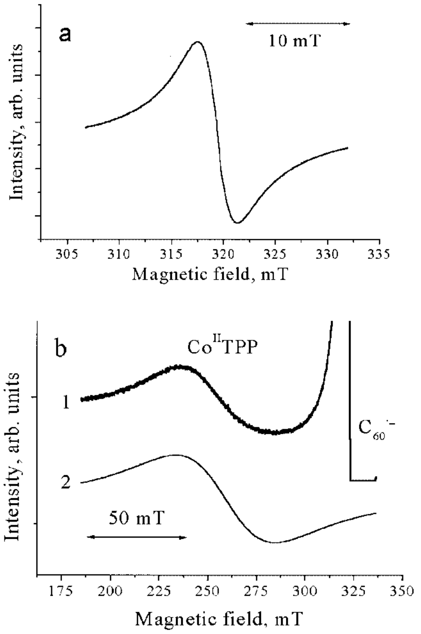

Figure 3. EPR spectrum of polycrystalline **1** at *T* = 290 K; (a) the signal attributable to $C_{60}^{\cdot-}$; (b) the signals attributable to $Co^{II}TPP$ and $C_{60}^{\cdot-}$ (1); the simulation of the signal from $Co^{II}TPP$ by one Lorentzian line is shown below (2)

and the line halfwidth becomes narrower ($g = 2.3785$ and $\Delta H = 41.5$ mT at 4 K).

When Rb was used instead of Cs, in the absence of CH_3CN, the complex $[(Rb^+)\cdot Co^{II}TPP\cdot(C_{60}^{\cdot-})]$ did not crystallize. We used the reaction of cationic metathesis to substitute the Rb^+ counter cations for other small cations such as Me_4N^+ (in **2**) and *N*-$MePy^+$ (in **3**). The crystallization of these complexes by the diffusion of *n*-hexane affords $[(Me_4N^+)\cdot(Co^{II}TPP\cdot C_{60}^-)\cdot(C_6H_5CN)\cdot(C_6H_4Cl_2)]$ (**2**), and $[(N\text{-}MePy^+)\cdot(Co^{II}TPP\cdot C_{60}^-)\cdot(C_6H_4Cl_2)_{1.2}]$ (**3**). The IR spectra of **2** and **3** justify their ionic ground state (the spectra manifest the absorption bands attributable to $C_{60}^{\cdot-}$) and show additional silent modes of C_{60} due to its symmetry breaking.[21] The EPR spectra of **2** and **3**, in contrast to **1**, show no signals from 290 down to 4 K indicating the formation of diamagnetic and EPR-silent σ-bonded $(Co^{II}TPP\cdot C_{60}^-)$ anions, which are stable in the 4−290 K range.

Thus, two extreme cases can be found in **1−3**. Complex **1** contains nonbonded $Co^{II}TPP$ and $C_{60}^{\cdot-}$ components in the 4−290 K range, whereas complexes **2** and **3** contain σ-bonded $(Co^{II}TPP\cdot C_{60}^-)$ anions stable in the 4−290 K range. Previously studied ionic $[\{Cr^I(C_6H_6)_2^{\cdot+}\}_{1.7}\cdot\{(Co^{II}TPP\cdot C_{60})_2\}^{1.7-}\cdot(C_6H_4Cl_2)_{3.3}]$[13] and $[(TDAE^{\cdot+})\cdot(Co^{II}TPP\cdot C_{60}^-)]$[16] are intermediates between **1**, and complexes **2** and **3**. At low temperatures they contain σ-bonded $[Co^{II}TPP\cdot C_{60}^-]$ anions. The broadening of the EPR signal above 200 K in $[\{Cr^I(C_6H_6)_2^{\cdot+}\}_{1.7}\cdot\{(Co^{II}TPP\cdot C_{60})_2\}^{1.7-}\cdot(C_6H_4Cl_2)_{3.3}]$ can be associated with the appearance of a small contribution from nonbonded $Co^{II}TPP$ and $C_{60}^{\cdot-}$.[16] Evident dissociation of σ-bonded $(Co^{II}TPP\cdot C_{60}^-)$ anions to nonbonded $Co^{II}TPP$ and $C_{60}^{\cdot-}$ components is observed in $[(TDAE^{\cdot+})\cdot(Co^{II}TPP\cdot C_{60}^-)]$ above 190 K, and it is accompanied by an increase of the magnetic moment, the essential broadening of the EPR line, and the shift of its *g*-factor to larger values. At 290 K approximately 20 % of total $Co^{II}TPP$ and $C_{60}^{\cdot-}$ exists in a nonbonded state.[16]

The temperature ranges of the existence of σ-bonded $(Co^{II}TPP\cdot C_{60}^-)$ anions in the ionic multi-component complexes of $Co^{II}TPP$ with C_{60}^- and the counter cations used are listed in Table 2. The complexes are given in Table 2 in order of increasing size of the counter cations. The increase in the size of counter cations is seen to destabilize the σ-bonded $[Co^{II}TPP\cdot C_{60}^-]$ anions. The use of large cations like Cs^+ solvated by one CH_3CN and nearly two C_6H_5CN molecules forces the units $Co^{II}TPP$ and $C_{60}^{\cdot-}$ apart, and does not allow them to approach each other so closely to form a $Co\cdots C(C_{60}^{\cdot-})$ σ-bond. Thus, in spite of the obvious ability of $Co^{II}TPP$ and $C_{60}^{\cdot-}$ to form σ-bonds, steric factors (namely, the size of the counter cations) also determine the possibility of the formation of σ-bonded $[Co^{II}TPP\cdot C_{60}^-]$ anions. Similarly, in ionic charge transfer complexes of C_{60} with metallocenes, the stability of single-bonded $[C_{60}^-]_2$ dimers varies in a wide range (the beginning of dissociation is in the 160−250 K range) and is determined by the size of the donor and even the solvent molecules involved in the complex.[20]

Experimental Section

General Remarks: $Co^{II}TPP$ and Me_4NI were purchased from Aldrich. *N*-MePyI was obtained by the reaction of Py with MeI and then recrystallized from *N*,*N*-dimethylformamide. C_{60} of 99.98 % purity was purchased from MTR Ltd. All solvents were distilled under argon: *o*-dichlorobenzene ($C_6H_4Cl_2$) over CaH_2, benzonitrile (C_6H_5CN) over Na/benzophenone under reduced pressure, acetonitrile over CaH_2, P_2O_5, and K_2CO_3. The solvents were degassed prior to use and were stored in a glove box. All manipulations during the synthesis and isolation of the crystals of **1−3** were carried out in a MBraun 150B-G glove box; the content of H_2O and O_2 was less than 1 ppm. The crystals were stored in the glove box and sealed in 2 mm quartz tubes for EPR measurements under 10^{-5} Torr. KBr pellets for IR measurements were also prepared in the glove box. UV-Vis-NIR spectra were measured on a Shimadzu-3100 spectrometer in the 240−2600 nm range. FT-IR spectra were measured with KBr pellets on a Perkin−Elmer 1000 Series spectrometer (400−7800 cm^{-1}). EPR spectra were recorded down to 4 K with a JEOL JES-TE 200 X-band ESR spectrometer equipped with a JEOL ES-CT470 cryostat.

Synthesis: The crystals of **1−3** were obtained by the diffusion of *n*-hexane into a solution containing the corresponding $[C_{60}^{\cdot-}\cdot Cation^+]$ salt and $Co^{II}TPP$ porphyrin complex. The diffusion was carried out in a glass tube of 1.5 cm in diameter and 40 mL volume with a ground glass plug. The crystals of **1−3** were formed as large black prisms of up to 1 × 1 × 0.5 mm^3. The composition of the compounds was determined from X-ray diffraction on a single crystal for **1** and by elemental analysis for **2** and **3** (Table 1). In **2** and **3**, the difference [(100 %)-(C, H, N, Cl, %)] exceeds the calculated content of metals (Co and Cr) indicating the addition of oxygen to the complexes during the elemental analysis. Indeed, the complexes are sensitive to oxygen. The addition of ap-

Table 2. The temperature ranges in which σ-bonded $(Co^{II}TPP\cdot C_{60}^-)$ anions exist in ionic multicomponent complexes

Complex	The temperature in which σ-bonded $(Co^{II}TPP\cdot C_{60}^-)$ anions exist, (K)	Counter cation
$\{(CH_3)_4N^+\}\cdot(Co^{II}TPP\cdot C_{60}^-)\cdot(C_6H_5CN)\cdot(C_6H_4Cl_2)$	4−290	$(CH_3)_4N^+$
$(N\text{-}MePy^+)\cdot(Co^{II}TPP\cdot C_{60}^-)\cdot(C_6H_4Cl_2)_{1.2}$	4−290	*N*-$MePy^+$
$\{Cr^I(C_6H_6)_2^{\cdot+}\}_{1.7}\cdot\{(Co^{II}TPP\cdot C_{60})_2\}^{1.7-}\cdot(C_6H_4Cl_2)_{3.3}$	4−290, probable appearance of contribution from nonbonded $Co^{II}TPP$ and $(C_{60}^{\cdot-})$ above 200 K	$Cr^I(C_6H_6)_2^{\cdot+}$
$(TDAE^{\cdot+})\cdot(Co^{II}TPP\cdot C_{60}^-)$	4−190	$TDAE^{\cdot+}$
$(Cs^+)\cdot Co^{II}TPP\cdot(C_{60}^{\cdot-})\cdot(C_6H_5CN)_{1.64}(C_6H_4Cl_2)_{0.36}\cdot CH_3CN$	does not exist	$(Cs^+)\cdot(C_6H_5CN)_{1.64}\cdot CH_3CN$

proximately one O_2 molecule per one formula unit of the complex is observed. Thus, the calculated C, H, N, and Cl (%) content was corrected for the composition (Formula unit:O_2). We assumed that oxygenation occurring during elemental analysis was extrinsic and omitted oxygen throughout the manuscript.

Complex 1: The cesium salt of fullerene $(Cs^+)\cdot(C_{60}^{\cdot-})$ was obtained by the dissolution of C_{60} (25 mg, 0.035 mmol) with Cs (5.2 mg, 0.038 mmol) in benzonitrile which was stirred for 2 hours at 60 °C. The purity of the salt was justified by the presence of characteristic $(C_{60}^{\cdot-})$ absorption bands in the solution NIR spectrum. The solution was cooled down to room temp. filtered, and $C_6H_4Cl_2$ and CH_3CN were added (the $C_6H_4Cl_2/C_6H_5CN/CH_3CN$ volume ratio is 50:45:5, the total volume is 20 mL). Co^{II}TPP (23.5 mg, 0.035 mmol) was dissolved in this solution at 60 °C; the resulting solution was cooled down to room temp., filtered into a glass tube and layered with *n*-hexane (20 mL). Crystals of **1** that precipitated after 1 month were washed with *n*-hexane and dried (yield 31 mg, 50 %).

Complexes 2 and 3: Complexes **2** and **3** were obtained similarly. The $(Rb^+)\cdot(C_{60}^{\cdot-})$ complex was obtained by the dissolution of C_{60} (100 mg, 0.14 mmol) with Rb (13.2 mg, 0.152 mmol) in benzonitrile (40 mL) at 60 °C by stirring for 2 hours. The solution was cooled down to room temp. and filtered. The purity of the $(Rb^+)\cdot(C_{60}^{\cdot-})$ salt was justified by the solution NIR spectrum. The solution 10 mL) containing of $(Rb^+)\cdot(C_{60}^{\cdot-})$ was treated with an excess of tetramethylammonium iodide (**2**) or *N*-methylpyridinium iodide (**3**) at 60 °C. After 4 hours the solution was cooled down, filtered, and mixed with $C_6H_4Cl_2$ at a 50:50 volume ratio (the total volume was 20 mL). Co^{II}TPP (23.5 mg, 0.035 mmol) was dissolved in the obtained solution at 60 °C, allowed to cool to room temp., filtered into a glass tube and layered with *n*-hexane (20 mL). Crystals of **2** and **3** that precipitated after 1 month were washed with *n*-hexane and dried (yield 30 mg, 50% for **2**; 34.6 mg, 60% for **3**).

X-ray Crystallographic Study: X-ray diffraction data were collected at 110 K on a Bruker SMART CCD diffractometer with an area detector (sealed tube, Mo-K_α radiation, $\lambda = 0.71073$ Å). A series of three ω scans with a 0.3° frame width were collected. Reflection intensities were integrated using the SAINT program.[25] The structure was solved with direct methods using SHELXTL program package[26] and refined by full-matrix least-squares on F^2. The ordered non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined within the "riding atom" model. Both C_6H_5CN molecules are statistically substituted by $C_6H_4Cl_2$ ones per 20 % and 16 %. One of the Co^{II}TPP phenyl rings is also disordered between two positions in a 40:60 ratio.

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[17] Crystallographic data for **1**: $C_{119.64}H_{40.64}Cl_{0.72}CoCsN_{6.64}$, M_r = 1788.23 g·mol^{-1}, black prisms, triclinic, $P\bar{1}$, a = 13.553(3), b = 14.096(4), c = 20.734(5) Å, α = 105.108(5), β = 106.148(5), γ = 92.160(5)°, V = 3642(1) Å^3, Z = 2, $d_{calcd.}$ = 1.631 g·cm^{-3}, T = 110 K, μ = 0.82 mm^{-1}, $F(000)$ = 1798, max. 2θ = 50.0°, R_{int} = 0.0338 for 30069 measured and 12793 unique reflections, $R[I > 2\sigma(I)]$ = 0.1215, wR_2 = 0.2731, GooF = 0.818. CCDC-224942 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223-336-033; E- mail: deposit@ccdc.cam.ac.uk].

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