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Fullerene complexes with cobalt(II) tetraphenylporphyrin: from molecular to ionic crystals

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ABSTRACT: The complexes of cobalt(II) tetraphenylporphyrin ($Co^{II}TPP$) with fullerenes C_{60}, C_{70} and $C_{60}(CN)_2$ are presented. It is shown that $Co^{II}TPP$ forms complexes with fullerenes in different solvents: [$Co^{II}TPP$·fullerene·solvent] (solvent = C_6H_6, C_6H_5Me, $C_6H_4Cl_2$, CS_2, $CHCl_3$). The use of additional donors (Cp_2Fe, $Cr^0(C_6H_6)_2$, and TDAE) in the synthesis of $Co^{II}TPP$/fullerene complexes allows one to obtain multi-component complexes ranging from neutral [$(Co^{II}TPP\cdot Py)_2\cdot Cp_2Fe\cdot$ fullerene·solvent] to ionic [$Co^{II}TPP\cdot(D_2^{\bullet+})\cdot$(fullerene$^{\bullet-}$)·solvent] ($D_2 = Cr^I(C_6H_6)_2$, TDAE). The interaction of $Co^{II}TPP$ with neutral and negatively charged fullerenes is considered. The neutral $Co^{II}TPP$/fullerene complexes are characterized by a secondary M...C(fullerene) bonding with the shortest Co...C contacts in the 2.69-2.82 Å range and noticeable changes in the electronic structure of the parent components. At the same time, σ-bonding is observed in ionic complexes between $Co^{II}TPP$ and fullerene radical anions with the shortened Co...C contacts being in the 2.28-2.32 Å range. The resulting ($Co^{II}TPP$·fullerene$^-$) anions are diamagnetic. The σ-bonding is relatively weak and the ($Co^{II}TPP$·fullerene$^-$) anions begin to dissociate above 200 K. Copyright © 2003 Society of Porphyrins & Phthalocyanines.

KEYWORDS: fullerenes, C_{60}, C_{70}, $C_{60}(CN)_2$, cobalt(II) tetraphenylporphyrin, donor-acceptor complexes, crystal engineering, crystal structures, σ-bonding.

INTRODUCTION

Fullerenes form complexes with numerous organic and organometallic donors ranging from aromatic hydrocarbons and amines to metallocenes and metalloporphyrins [1-3]. The latter family of complexes is of great interest because of their promising photoactive properties [4]. Metalloporphyrins can be used to determine molecular structures of endohedral metallofullerenes [5] and chemically modified fullerenes [6]. Appended porphyrins can be used as chromatographic materials for fullerene separation [7]. Crystal structures of porphyrin/fullerene complexes can help to understand the porphyrin/fullerene interaction in a chromatographic column and to optimize the process.

More than fifty fullerene/metalloporphyrin complexes have been described to date. Among these are fullerene complexes with metal octaethylporphyrins [6], tetraphenylporphyrins [8-11], and porphyrazines [12], as well as covalently and coordinatively linked metalloporphyrin dimers [13, 14]. Different chemically modified porphyrins in which two porphyrin moieties bonded by either one ("jaw" porphyrins [15]) or two bridged chains (cyclic dimers [16]) were used for the preparation of complexes with fullerenes. These molecules have a high affinity to fullerenes [15, 16].

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In this paper we present the results obtained on fullerene complexes with cobalt(II) tetraphenylporphyrin ($Co^{II}TPP$), which forms a large variety of complexes due to a possible incorporation of additional donor molecules into the $Co^{II}TPP$/fullerene framework. Because of different donor strengths of the incorporated molecules, it becomes possible to design unusual multi-component complexes ranging from neutral to ionic ones and to then study the interaction of $Co^{II}TPP$ with neutral and negatively charged fullerenes.

RESULTS AND DISCUSSION

The resulting complexes are listed in Table 1. The syntheses of these complexes were described elsewhere [8-11, 17-21].

Neutral complexes

$Co^{II}TPP$ forms complexes with fullerenes C_{60}, C_{70}, $C_{60}CN_2$ in different solvents (CS_2, $C_6H_4Cl_2$, C_6H_5Me) (Table 1). Some of these solvent molecules are involved in the crystal structure. The crystal structure of $Co^{II}TPP{\cdot}C_{60}{\cdot}(C_6H_4Cl_2)_{2.5}$ (**1**) determined from X-ray analysis shows the presence of vacancies in the $Co^{II}TPP$/fullerene framework which accomodate the $C_6H_4Cl_2$ molecules (Fig. 1). Probably because of a loose arrangement of these molecules in the vacancies, they are removed from the crystals under storage and the crystals decompose. Similarly the crystals of **2** and **5** are also unstable upon storage due to the loss of solvent.

According to the IR and UV-vis-NIR spectra of **1**-**7**, they have a neutral ground state [10, 17]. However, a noticeable interaction of the π-system of fullerenes with the *d*-π system of $Co^{II}TPP$ is observed. The EPR spectra of **1**, **3**, **4**, and **7** reveal only one unpaired electron per formula unit localized on $Co^{II}TPP$ with S = 1/2 ground state [10, 17]. The EPR spectra of the $Co^{II}TPP$/fullerene complexes ($g_\perp$ = 2.51-2.64 and $g_{//}$ = 2.28-2.42 at room temperature (RT = 290 K)) are essentially different from that of parent $Co^{II}TPP$ ($g_\perp$ = 3.322 and $g_{//}$ = 1.798 [22]) due to the changes in the hyperfine interaction parameters, which are the most sensitive to the local environment of the metal center and are similar to those of the $Co^{II}TPP{\cdot}A$ compounds

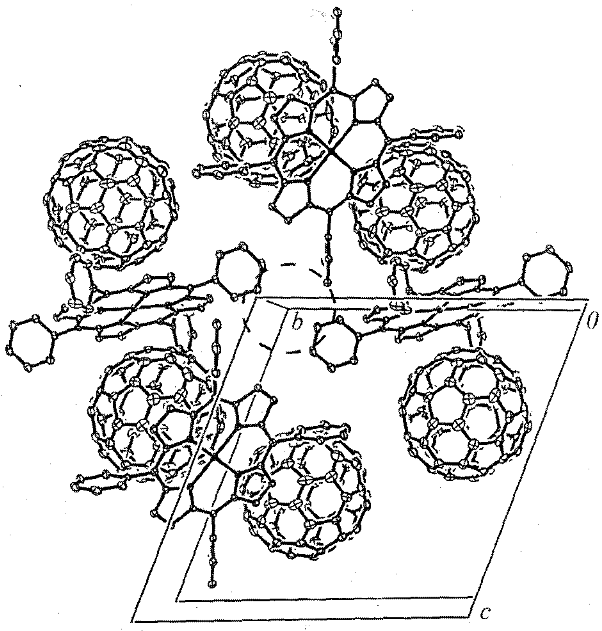

Fig. 1. The fragment of crystal structure of $Co^{II}TPP{\cdot}C_{60}{\cdot}(C_6H_4Cl_2)_{2.5}$ (**1**). The vacancies shown by the dashed circles are occupied by the $C_6H_4Cl_2$ molecules (not depicted) [17]

Table 1. Complexes of $Co^{II}TPP$ with fullerenes C_{60}, C_{70} and $C_{60}CN_2$

Compound	Type of the complex	Composition	Reference
1	neutral	$Co^{II}TPP{\cdot}C_{60}{\cdot}(C_6H_4Cl_2)_{2.5}$	[17]
2	neutral	$Co^{II}TPP{\cdot}C_{60}{\cdot}C_6H_5Me$	[17]
3	neutral	$Co^{II}TPP{\cdot}C_{60}{\cdot}(CS_2)_{0.5}$	[8, 10, 11]
4	neutral	$Co^{II}TPP{\cdot}C_{70}{\cdot}(CHCl_3)_{1.3}{\cdot}(C_6H_6)_{0.2}$	[17]
5	neutral	$Co^{II}TPP{\cdot}C_{70}{\cdot}(C_6H_4Cl_2)_{2.5}$	[17]
6	neutral	$Co^{II}TPP{\cdot}C_{70}$	[8, 10, 11]
7	neutral	$Co^{II}TPP{\cdot}C_{60}(CN)_2{\cdot}(C_6H_5Me)_{2.5}{\cdot}(CHCl_3)_{1.5}$	[17]
8	neutral multi-component	$Cp_2Fe{\cdot}(Co^{II}TPP{\cdot}Py)_2{\cdot}C_{60}{\cdot}C_6H_5Me$	[18]
9	ionic multi-component	$[Cr^I(C_6H_6)_2]_{1.7}{\cdot}(Co^{II}TPP)_2{\cdot}(C_{60})_2{\cdot}(C_6H_4Cl_2)_{3.3}$	[17]
10	ionic multi-component	$TDAE{\cdot}Co^{II}TPP{\cdot}C_{60}$	[21]
11	ionic multi-component	$[Cr^I(C_6H_6)_2]{\cdot}Co^{II}TPP{\cdot}(C_{70})_2{\cdot}(C_6H_4Cl_2)_2$	[17]
12	ionic multi-component	$[Cr^I(C_6H_6)_2]_2{\cdot}Co^{II}TPP{\cdot}[C_{60}(CN)_2]_2{\cdot}(C_6H_4Cl_2)_3$	[17, 19, 20]

with strongly coordinated ligands: CO, $P(OCH_3)_3$, and py. These compounds have asymmetric spectra with $g_{//} = 2.017$-2.027 and $g_{\perp} = 2.17$-2.32 in solution [23].

Shortened contacts are formed in **1** and **4** between cobalt (by η^2-type) or nitrogen atoms of $Co^{II}TPP$ and C_{60} or C_{70} carbons (the d-π and π-π interaction, respectively) [17]. The Co...C(C_{60}) (or Co...C(C_{70})) contacts of 2.69-2.75 Å in **1** (Fig. 2 a) and **4** are close to those in various neutral C_{60} and C_{70} complexes with cobalt-containing tetraaryl- and octaethylporphyrins: 5,10,15,20-tetrakis(3,5-(di-*tret*-butyl)phenyl)-21*H*, 23*H*-porphyrin cobalt(II) - $Co^{II}TBP{\cdot}C_{60}$ - 2.61 Å [24], 5,10,15,20-tetrakis(*p*-methoxyphenyl)-21*H*,23*H*-porphyrin cobalt(II) - $Co^{II}TMPP{\cdot}(C_{60})_2{\cdot}(C_6H_5Me)_3$ - 2.64 Å [18], and 2,3,7,8,12,13,17,18-octaethylporphyrin cobalt(II) - $(Co^{II}OEP)_2{\cdot}C_{60}{\cdot}CHCl_3$ - 2.74 Å [6], and $Co^{II}OEP{\cdot}C_{70}{\cdot}C_6H_6{\cdot}CHCl_3$ - 2.80 Å [6]. These contacts are shorter than the non-bonded Van-der-Waals contacts (3.1-3.3 Å) but are significantly longer than strong η^2-coordination (2.1-2.2 Å) and can be described as a secondary bonding.

A red shift of the Soret and Q-bands of $Co^{II}TPP$ is observed in the UV-vis-NIR spectra of **1-7** relative to those of parent $Co^{II}TPP$ [10, 17]. Similar shifts were reported for the $Co^{II}TPP{\cdot}A$ compounds [23]. These shifts are common upon coordination of different ligands (including fullerenes) to $Co^{II}TPP$.

Thus, the characteristic features of the $Co^{II}TPP$ complexes with fullerenes are secondary M... C(fullerene) bonding with the shortest Co...C contacts in the 2.69-2.75 Å range and minor changes in the electronic structure of parent $Co^{II}TPP$. The complexes **1-7** have a neutral ground state. The absence of noticeable charge transfer from $Co^{II}TPP$ to fullerenes is associated with weak donor properties of $Co^{II}TPP$ ($E^{+/0}$ of $Co^{II}TPP$ is +0.52 V [25] relative to those of the fullerenes ($E^{0/-}$ of C_{60} and C_{70} = -0.44 and -0.41 V [26] and $E^{0/-}$ of $C_{60}(CN)_2$ = -0.25 V [27]).

Neutral multi-component complexes

An interesting feature of $Co^{II}TPP{\cdot}C_{60}{\cdot}(C_6H_4Cl_2)_{2.5}$ (**1**) is the presence of vacancies in the crystal structure (Fig. 1). Such vacancies are probably formed due to the packing of planar porphyrin molecules and spherical fullerene ones. Even $C_6H_4Cl_2$ solvent molecules are rather loosely arranged in these vacancies and can be removed from the crystals.

The large size of the vacancies in the $Co^{II}TPP$/fullerene framework allows another small molecule to be incorporated. Ferrocene (Cp_2Fe) has a small size comparable with that of $C_6H_4Cl_2$ molecules and donor properties stronger than those of $Co^{II}TPP$ ($E^{+/0}$ of Cp_2Fe is +0.40 V [2]). The preparation of $Co^{II}TPP$ complex with C_{60} in the presence of pyridine and an excess of ferrocene results in the formation of multi-component $(Co^{II}TPP{\cdot}Py)_2{\cdot}C_{60}{\cdot}Cp_2Fe{\cdot}C_6H_5Me$ (**8**) [18]. There are two types of vacancies in this complex. Planar and smaller vacancies (distorted squares with diagonals of ca. 7.5 × 6 Å and a thickness of ca. 3.4 Å) are occupied by C_6H_5Me molecules, whereas larger and bulkier vacancies (almost spherical with a diameter of ca. 6.8 Å) accommodate ferrocene molecules (Fig. 3).

The donor strength of ferrocene is still not high enough to ionize C_{60} in the solid state and according to the IR- and UV-vis-NIR spectra the complex has a neutral ground state [18]. The role of ferrocene in this complex is only to occupy bulky vacancy and stabilize this crystal structure.

The cobalt atom of $Co^{II}TPP$ in **8** is coordinated with pyridine and TPP in a flattened square-pyramidal manner, deviating by 0.190 Å from the mean plane of the macrocycle towards the Py ligand. The C_{60} molecules arrange near the metal atoms at the apical site opposite to the Py ligand. Slightly shortened Co···C(C_{60}) contacts of 2.82 Å (Fig. 2b) involve a carbon atom of the 5-6 bond of C_{60}, which is almost parallel to the N-Co-N line in the $Co^{II}TPP$ molecule. These contacts are close to similar contacts found

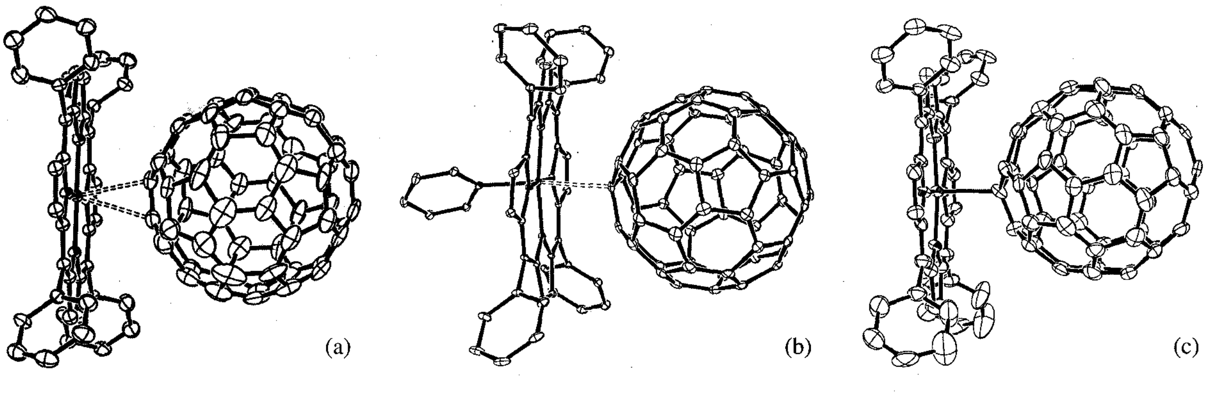

Fig. 2. Different types of $Co^{II}TPP$/fullerene interaction in: (a) $Co^{II}TPP{\cdot}C_{60}{\cdot}(C_6H_4Cl_2)_{2.5}$ (**1**) [17]; (b) $Cp_2Fe{\cdot}(Co^{II}TPP{\cdot}Py)_2{\cdot}C_{60}{\cdot}C_6H_5Me$ (**8**) [18]; (c) $[Cr^I(C_6H_6)_2]_{1.7}{\cdot}(Co^{II}TPP{\cdot}C_{60})_2{\cdot}(C_6H_4Cl_2)_{3.3}$ (**9**) [17]. The shortened Van-der-Waals contacts (<3.0 Å) and the σ-bonding are shown by dashed and full lines, respectively

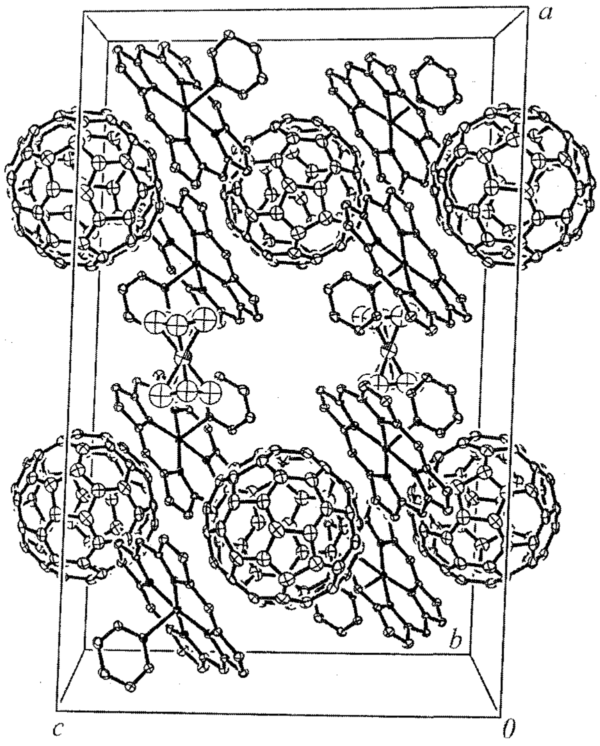

Fig. 3. The fragment of crystal structure of $Cp_2Fe\cdot(Co^{II}TPP\cdot Py)_2\cdot C_{60}\cdot C_6H_5Me$ (**8**). The vacancies occupied by Cp_2Fe molecules are shown. The phenyl substituents of $Co^{II}TPP$ and C_6H_5Me molecules are not shown. From reference 18 with permission

in other fullerene complexes with Co^{II}-containing porphyrins (see above).

Ionic multi-component complexes

Bis(benzene)chromium ($Cr^0(C_6H_6)_2$) and tetrakis-(dimethylamino)ethylene (TDAE) have essentially stronger donor properties ($E^{+/0}$ = -0.72 V [28], and -0.75 V [2]) in contrast to Cp_2Fe and can ionize fullerenes to radical-anions. Indeed, $[Cr^0(C_6H_6)_2]$ and TDAE form ionic CT complexes with fullerene C_{60}: $(Cr^I(C_6H_6)_2{}^{\bullet+})(C_{60}{}^{\bullet-})$ [29, 30], $(TDAE^{\bullet+})(C_{60}{}^{\bullet-})$ [31] and $C_{60}(CN)_2$: $(Cr^I(C_6H_6)_2{}^{\bullet+})\cdot(C_{60}(CN)_2{}^{\bullet-})\cdot C_6H_6$ [27]. The sizes of the $Cr^0(C_6H_6)_2$ and TDAE molecules are also comparable with those of the solvent and allow these donors to be incorporated into the $Co^{II}TPP$/fullerene framework to form ionic multi-component $(D_2{}^{\bullet+})\cdot Co^{II}TPP\cdot(\text{fullerene}^-)\cdot$solvent complexes, where D_2 are $Cr^0(C_6H_6)_2$ and TDAE .

According to the UV-vis-NIR spectra of **9-12,** they contain $Cr^I(C_6H_6)_2{}^{\bullet+}$ and $TDAE^{\bullet+}$ radical cations and corresponding fullerene radical anions [17, 21]. The X-ray diffraction analysis of **9** and **12** [17, 19, 20] shows that C_{60} anions are σ-bound with $Co^{II}TPP$ in **9** (Fig. 2c), whereas only one of two $C_{60}(CN)_2$ anions has such coordination in **12.** The σ-bonded $(Co^{II}TPP\cdot C_{60}{}^-)$ anions in **9** form a cage structure with large cavities connected through channels along the *b*-axis. The walls of each cavity are built of six $(Co^{II}TPP\cdot C_{60}{}^-)$ units. The cavities accommodate both $C_6H_4Cl_2$ and $Cr^I(C_6H_6)_2{}^{\bullet+}$ (Fig. 4).

In accordance with the X-ray diffraction data, the ionic formulas of **9** and **12** are: $[Cr^I(C_6H_6)_2{}^{\bullet+}]_{1.7}\cdot[(Co^{II}TPP\cdot C_{60})_2]^{1.7-}\cdot(C_6H_4Cl_2)_{3.3}$ (**9**), and $[Cr^I(C_6H_6)_2{}^{\bullet+}]_2\cdot[Co^{II}TPP\cdot C_{60}(CN)_2{}^-]\cdot(C_{60}(CN)_2{}^{\bullet-})\cdot(C_6H_4Cl_2)_3$ (**12**). Complex **11** has a composition similar to that of **12** and by analogy must have the ionic formula: $[Cr^I(C_6H_6)_2{}^{\bullet+}]_2\cdot(Co^{II}TPP\cdot C_{70}{}^-)\cdot(C_{70}{}^{\bullet-})\cdot(C_6H_4Cl_2)_2$ (**11**). A number of spins estimated from magnetic susceptibility of these complexes at RT is essentially smaller than that expected from their composition ($Co^{II}TPP$, $Cr^I(C_6H_6)_2{}^{\bullet+}$, and $(\text{fullerenes}^{\bullet-})$ formally have S = 1/2 ground state). The magnetic moment of **9** (2.4 μ_B) is close to a noninteracting 1.7 S = 1/2 system (μ_{eff} of 2.26 μ_B). Since the EPR signal of **9** (g = 1.986) is characteristic of $Cr^I(C_6H_6)_2{}^{\bullet+}$ [32], it is deduced that these spins are localized mainly on $Cr^I(C_6H_6)_2{}^{\bullet+}$. RT magnetic susceptibilities of **11** and **12** of 2.91-2.98 μ_B are defined by three non-interacting spins per formula unit (spin-only value is 3.00 μ_B). The EPR signal of **11** has two components at RT, whereas that of **12** is split into two components below 180 K. These two components can be attributed to $Cr^I(C_6H_6)_2{}^{\bullet+}$ and non-bonded $(\text{fullerene}^{\bullet-})$. Therefore, three spins per formula unit are basically localized in **11**

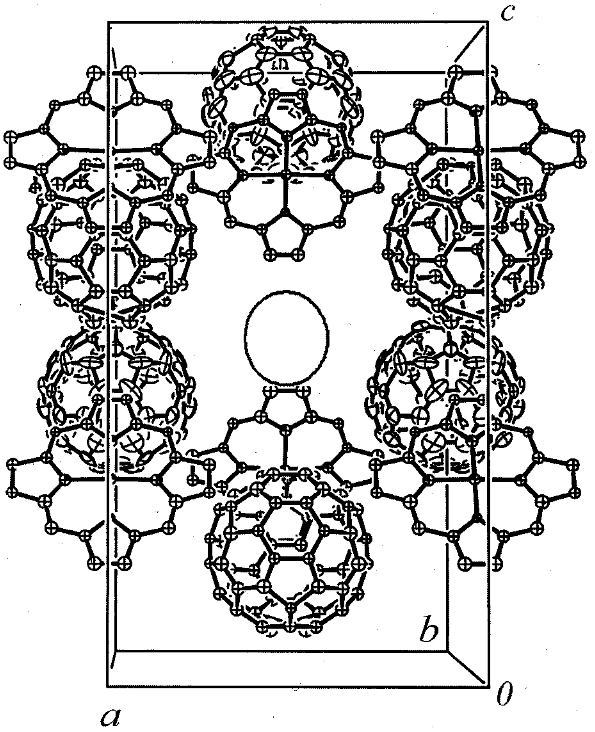

Fig. 4. The fragment of crystal structure of $(Cr^I(C_6H_6)_2)_{1.7}\cdot(Co^{II}TPP\cdot C_{60})_2\cdot(C_6H_4Cl_2)_{3.3}$ (**9**) [17]. The cavities connected by the through channel are shown by circle. The phenyl substituents of $Co^{II}TPP$, $Cr^I(C_6H_6)_2$ and $C_6H_4Cl_2$ molecules are omitted

and **12** on $Cr^{I}(C_6H_6)_2^{\bullet +}$ and non-bonded fullerene$^{\bullet -}$. Consequently, all σ-bonded (Co^{II}TPP·fullerene^{-}) anions in **9, 11, 12** are deduced to be diamagnetic.

Complex **10** formally contains three paramagnetic species with spin S = 1/2 (Co^{II}TPP, $TDAE^{\bullet +}$ and $C_{60}^{\bullet -}$); thus, a magnetic moment of 3 μ_B is expected. However, the observed magnetic moment (only 1.45 μ_B) is even smaller than 1.73 μ_B calculated for a non-interacting S = 1/2 system [21]. The EPR spectrum of **10** is a single Lorentzian line in the 4-190 K range with g = 2.0030-2.0050 and nearly constant ΔH of 3.2 mT. This signal can be attributed to $TDAE^{\bullet +}$ (g = 2.0035 [33]). These data allow one to conclude that spin density in **10** is mainly localized on $TDAE^{\bullet +}$ and the formation of σ-bonded diamagnetic ($Co^{II}TPP{\cdot}C_{60}^{-}$) anions in the 4-190 K range can also be suggested: ($TDAE^{\bullet +}$)($Co^{II}TPP{\cdot}C_{60}^{-}$) (**10**).

The Co...C(fullerene) distances in the σ-bonded (Co^{II}TPP·fullerene^{-}) anions in **9** and **12** are in the 2.28-2.32 Å range. These distances are longer than those in the strong covalent Co...C σ-bond in alkylcobalamins (1.99-2.03 Å [34]) but are essentially shorter than the M...C(fullerene) distances (in the 2.61-3.00 Å range) in the neutral complexes of fullerenes with metal-containing tetraphenyl- and octaethylporphyrins [6, 9, 10-12, 17, 18]. Thus, it is shown that fullerene radical anions are able to be essentially stronger bound with Co^{II}TPP than neutral fullerenes. At the same time the observed σ-bond in Co^{II}TPP/fullerene complexes is weaker than the strong Co...C σ-bond and the dissociation of this bond in $Co^{II}TPP{\cdot}C_{60}^{-}$ anions is possible at high temperature.

Indeed, above 190 K the magnetic moment of **10** increases with temperature up to 1.85 μ_B at 300 K [21], possibly due to a contribution from the emerging paramagnetic Co^{II}TPP and $C_{60}^{\bullet -}$ components into total magnetic susceptibility of **10**. The appearance of a contribution from paramagnetic Co^{II}TPP and $C_{60}^{\bullet -}$ components is supported by the EPR data. Above 190 K the signal essentially broadens and shifts to larger g-factors (g = 2.0194 and ΔH = 24.2 mT at RT) [21].

$$\underset{\text{diamagnetic, EPR silent}}{\sigma\text{-bonded }(Co^{II}TPP{\cdot}C_{60}^{-})} \xrightleftharpoons{190\text{ K}} \underset{\text{paramagnetic, EPR active}}{\text{nonbonded }Co^{II}TPP\text{ and }C_{60}^{\bullet -}}$$

A small increase in the magnetic moments and the broadened EPR signals above 200 K were also observed in **9** and **12** [17, 19, 20]. This can also be attributed to the appearance of a small contribution from nonbonded Co^{II}TPP and $C_{60}^{\bullet -}$ or $C_{60}(CN)_2^{\bullet -}$. However, this effect is weaker in **9** and **12** than in **10**.

CONCLUSION

Different neutral Co^{II}TPP/fullerene complexes can be obtained depending on the solvent used. The presence of vacancies in some of these complexes allows one to incorporate additional donor molecules and develop the multi-component complexes of general composition: $D_2{\cdot}Co^{II}$TPP·fullerene·solvent, where D_2 is Cp_2Fe, $Cr^{I}(C_6H_6)_2$ and TDAE. The D_2 and solvent molecules are accomodated in large vacancies or channels in the Co^{II}TPP and fullerenes cage framework. D_2 molecules affect charged state of fullerenes and these complexes can range from neutral (Cp_2Fe) to essentially ionic species ($Cr^{I}(C_6H_6)_2$, TDAE). The interaction of neutral fullerenes with Co^{II}TPP is characterized by secondary M...C(fullerene) bonding with the shortest Co...C contacts in the 2.69-2.82 Å range and noticeable changes in the electronic structure of parent components. The interaction of negatively charged fullerenes with Co^{II}TPP is essentially different. The shortened Co...C contacts of 2.28-2.32 Å indicate σ-bonding between Co^{II}TPP and fullerene radical anions and the resulting (Co^{II}TPP·fullerene^{-}) anions are diamagnetic. The σ-bonding in (Co^{II}TPP·fullerene^{-}) anions is relatively weak and they can dissociate above 200 K.

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