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First ionic multi-component complex of fullerene $C_{60}(CN)_2$ with Co(II)tetraphenylporphyrin and bis(benzene)chromium[☆]

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Abstract

First ionic multi-component complex $CoTPP\cdot 2C_{60}(CN)_2\cdot 2Bz_2Cr\cdot 3C_6H_4Cl_2$ (CoTPP: cobalt(II)tetraphenylporphyrin; Bz_2Cr: bis(benzene)chromium; $C_6H_4Cl_2$: *o*-dichlorobenzene) has been synthesized. CoTPP molecules and fullerides form channels providing the accommodation of $Bz_2Cr^{\bullet +}$ and $C_6H_4Cl_2$. For the first time it is shown that, in contrast to the neutral fullerenes, the cobalt atom of CoTPP coordinates to the fullerene anions with short Co···C(fullerene) distance of 2.28 Å. CoTPP–$C_{60}(CN)_2{}^-$ anion is diamagnetic according to the EPR- and SQUID-measurements. The shape of the starting molecule retains at the formation of the $C_{60}(CN)_2{}^{\bullet -}$ anion-radicals. The length of C≡N bonds are 1.143 and 1.161 Å.

Keywords: Multi-component complexes; Fullerides; Porphyrins; Bis(benzene)chromium

1. Introduction

Ionic complexes of fullerenes are of great interests due to intriguing physical and structural properties [1,2]. Unfortunately the number of donor compounds able to reduce fullerenes is restricted by their weak acceptor properties [3]. The design of multi-component complexes $[D_1(\text{fullerene}^-\cdot D_2{}^+)]$, where D_1 is large structure-forming molecule and D_2 is a small molecule with strong donor properties can essentially extend the number of ionic complexes of fullerenes. Previously, the neutral complexes containing cobalt and zinc tetraphenylporphyrins CoTPP·Py and ZnTPP·Py (Py: pyridine) and ferrocene were obtained [4]. Bz_2Cr is the most suitable as D_2 component for the preparation of the ionic complexes of fullerenes [5]. It has a small size together with strong donor property ($E_{1/2}^{+/0} = -0.72$ V versus SCE [5], calculated -1.12 V versus Fc/Fc^+) which is enough for the reduction of $C_{60}(CN)_2$ to monoanionic state ($E_{1/2}^{0/-} = -0.935$ V versus Fc/Fc^+ [6]). In this paper, the first ionic multi-component complex $CoTPP\cdot 2C_{60}(CN)_2\cdot 2Bz_2Cr\cdot 3C_6H_4Cl_2$ (**1**) is characterized and its crystal structure is presented.

2. Experiment

Fullerene, CoTPP and Bz_2Cr were dissolved in 1:1:1.8 molar ratio in $C_6H_4Cl_2$. The hexane was layered over the obtained solution. Two solutions were allowed to diffuse together over 1 month and the crystals of **1** were formed with 50–70% yield. All manipulations were carried out in the atmosphere of inert gas in a glove box. The crystal data for **1** are: $C_{207}H_{62}N_8Cl_5CoCr_2$, triclinic, $P\bar{1}$, $a = 13.967(1)$ Å, $b = 15.928(1)$ Å, $c = 30.332(2)$ Å, $\alpha = 92.30(1)$, $\beta = 100.89(1)$, $\gamma = 103.46(1)^\circ$, $Z = 2$, $V = 6419.6(3)$ Å^3, $D_c = 1.546$ g cm^{-3}, $T = 120$ K, 21169 unique reflections, $R_1 = 0.079$, and $wR_2 = 0.210$.

3. Results and discussion

The main building block of **1** is $2C_{60}(CN)_2\cdot CoTPP$ unit (Fig. 1). One $C_{60}(CN)_2$ (**A**) in the unit is covalently bonded to CoTPP with the Co···C distance of 2.28 Å, whereas, the second $C_{60}(CN)_2$ (**B**) forms van der Waals contacts with CoTPP by η^2-type (the Co···C distances of 2.79 and 2.93 Å). The 1:1 molar ratio of Bz_2Cr and $C_{60}(CN)_2$ in **1** yields the

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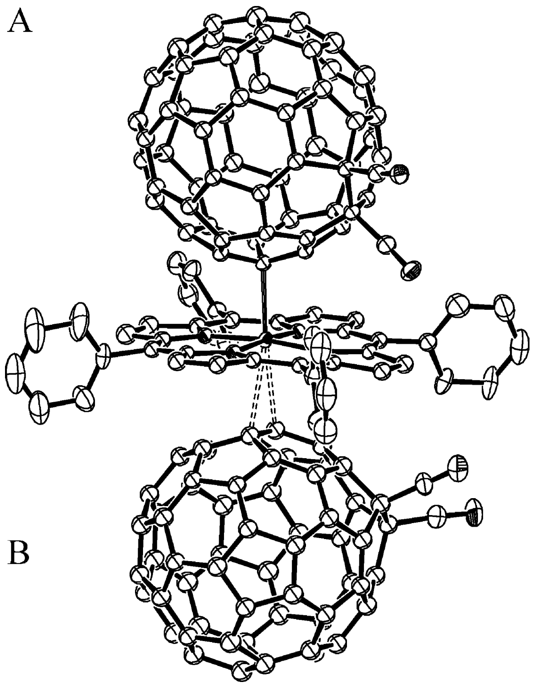

Fig. 1. The shortened van der Waals contacts and the η^1-coordination of CoTPP with $C_{60}(CN)_2^-$ (dashed and thin lines, respectively).

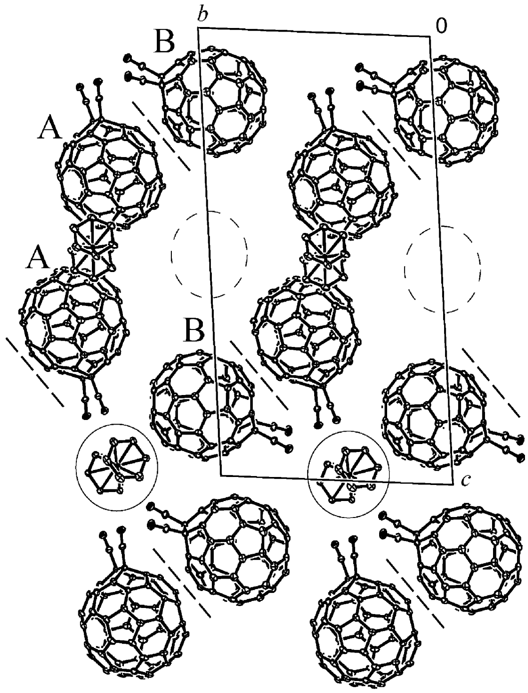

Fig. 2. The view of the packing of $C_{60}(CN)_2^-$ and $Bz_2Cr^{\bullet+}$ along the *a*-axis. The positions of the CoTPP molecules are shown by dashed lines. The ellipses show the channels I and II (thin and dashed lines, respectively).

-1 formal charge on the $C_{60}(CN)_2$ molecules. Indeed the bands in the IR-spectrum of **1** correspond to the formation of $Bz_2Cr^{\bullet+}$ and $C_{60}(CN)_2^-$ ions. The band of $C_{60}(CN)_2$ at 1430 cm^{-1} which is the most sensitive to the charge transfer to the molecule shifts to 1391 cm^{-1}. The shift of the band of C≡N vibration from 2242 to 2230 cm^{-1} also corresponds to the increase of electron density on the C≡N fragments. Thus, the ionic formula of **1** is $(CoTPP–C_{60}(CN)_2^-$ (**A**))$(C_{60}(CN)_2^{\bullet-}$·(**B**))·$2(Bz_2Cr^{\bullet+})\cdot 3C_6H_4Cl_2$. In UV-vis–NIR spectrum of **1** in KBr matrix, along with the bands of neutral CoTPP at 427 and 533 nm and those of $C_{60}(CN)_2$ at 261 and 326 nm, new bands appear in NIR-range at 1049 nm (the intra-molecular transition in $C_{60}(CN)_2^{\bullet-}$) and at 1200 nm (the charge transfer in CoTPP–$C_{60}(CN)_2^-$ anion or between $C_{60}(CN)_2^-$ anion-radicals).

Complex **1** is an unique example of the cage structure with large channels accommodating guest molecules ($Bz_2Cr^{\bullet+}$ and $C_6H_4Cl_2$). Two types of channels with different sizes are formed along the *a*-axis (Fig. 2). The channel I is occupied by the ordered $Bz_2Cr^{\bullet+}$. Negatively charged C≡N groups of four $C_{60}(CN)_2^-$ direct to this $Bz_2Cr^{\bullet+}$ (Fig. 2) forming several N···C(Bz_2Cr) contacts in the 3.20–3.25 Å range. The channel II has the larger size than I because its walls additionally contain ordered $Bz_2Cr^{\bullet+}$. The channel contains the strongly disordered $Bz_2Cr^{\bullet+}$ and $C_6H_4Cl_2$. Their disorder is associated with the absence of any shortened contacts with fullerenes. The fullerene molecules have several shortened contacts to one another (3.17–3.40 Å).

The non-interacting $C_{60}(CN)_2^{\bullet-}$ 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 are averaged to 1.39 and 1.45 Å, respectively, and are close to those for the neutral molecule [6]. The retention of $C_{60}(CN)_2$ shape may be attributed to the non-degenerated LUMO orbital [7] and the absence of Jahn–Teller effect. The C≡N bonds are 1.143(6) and 1.161(6) Å.

The magnetic susceptibility of **1** at room temperature (RT) ($\mu_{eff} = 2.91\ \mu_B$) is defined by the spins from $Bz_2Cr^{\bullet+}$ and the non-bonded $C_{60}(CN)_2^{\bullet-}$ (three non-interacting spins per formula unit give μ_{eff} value is equal to 3.0 μ_B). This implies that CoTPP–$C_{60}(CN)_2^-$ units are diamagnetic. The EPR signal has $g = 1.991$ with $\Delta H = 110$G at RT and splits into two components below 180 K with $g_1 = 1.996$ and $g_2 = 1.988$ with $\Delta H = 16$ and 19G, respectively. Two components may be attributed to two different signals from $Bz_2Cr^{\bullet+}$ (g_2) [8] and the resonating one (g_1) between $C_{60}(CN)_2^{\bullet-}$ and $Bz_2Cr^{\bullet+}$. The latter signal is characteristic of a strong exchange coupling and has the mean *g*-factor value between those for $C_{60}(CN)_2^{\bullet-}$ and $Bz_2Cr^{\bullet+}$.

4. Conclusion

Two of the most characteristic features of the title complex are the σ-bonding between Co and one of two $C_{60}(CN)_2^-$ and the completely ionic ground state of $(CoTPP–C_{60}(CN)_2^-)$ $(C_{60}(CN)_2^{\bullet-})\cdot 2(Bz_2Cr^{\bullet+})\cdot 3C_6H_4Cl_2$. The formation of weak covalent bond is probably associated with the appearance of the additional electron on π^*-level of $C_{60}(CN)_2^-$. Thus, the fullerenes anions also may be the ligands for d-metal containing compounds like CO, and NO [9].

The complex is a paramagnet with negative Weiss constant ($\Theta = -2.4$ K). This is attributed to the magnetic dilution of paramagnetic $Bz_2Cr^{\bullet+}$ and the non-bonded $C_{60}(CN)_2^{\bullet-}$ by the diamagnetic CoTPP–$C_{60}(CN)_2^-$ units. The complex has RT conductivity of 4×10^{-5} S cm^{-1} which is characteristic of fullerene containing salts with bulky cations [2]. At the same time **1** may have interesting photoactive properties as an analog of the dyad molecules: porphyrin–C_{60}.

Acknowledgements

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