Charge transfer complexes of fullerenes containing \(C_{60}^{\cdot -}\) and \(C_{70}^{\cdot -}\) radical anions with paramagnetic Co\(III\)(dppe)\(_2\)Cl\(+\) cations (dppe: 1,2-bis(diphenylphosphino)ethane)†

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The reduction of Co\(III\)(dppe)Cl\(_2\) with sodium fluorenone ketyl produces a red solution containing the Co\(^{II}\) species. The dissolution of C\(_{60}\) in the obtained solution followed by the precipitation of crystals with hexane yields a salt \((\text{Co(dppe)}_2^{\cdot -})(\text{C}_{60}^{\cdot -})\cdot 2\text{C}_6\text{H}_4\text{Cl}_2\) and a novel complex \((\text{Co(dppe)}_2\text{Cl})(\text{C}_{60})\) (1). With C\(_{70}\), only the crystals of \((\text{Co(dppe)}_2\text{Cl})(\text{C}_{70})\cdot 0.5\text{C}_6\text{H}_4\text{Cl}_2\) (2) are formed. Complex 1 contains zig-zag fullerene chains whereas closely packed double chains are formed from fullerenes in 2. According to the optical spectra and magnetic data charge transfer occurs in both 1 and 2 with the formation of the Co\(^{III}\)(dppe)\(_2\)Cl\(^+\) cations and the C\(_{60}^{\cdot -}\) or C\(_{70}^{\cdot -}\) radical anions. In spite of the close packing in crystals, C\(_{60}^{\cdot -}\) or C\(_{70}^{\cdot -}\) retain their monomeric form at least down to 100 K. The effective magnetic moments of 1 and 2 of 1.98 and 2.27\(\mu_B\) at 300 K, respectively, do not attain the value of 2.45\(\mu_B\) expected for the system with two non-interacting \(S = 1/2\) spins at full charge transfer to fullerenes. Most probably di- and tri- magnetic (Co\(^{III}\)(dppe)\(_2\)Cl\(^2-\)) and neutral fullerenes are partially preserved in the samples which can explain the weak magnetic coupling of spins and the absence of fullerene dimerization in both complexes. The EPR spectra of 1 and 2 show asymmetric signals approximated by several lines with \(g\)-factors ranging from 2.0099 to 2.3325. These signals originate from the exchange interaction between the paramagnetic Co\(^{III}\)(dppe)\(_2\)Cl\(^+\) cations and the fullerene\(^{\cdot -}\) radical anions.

Introduction

Ionic compounds of fullerenes possess promising conducting and magnetic properties.1–4 Crystalline samples of these compounds are generally prepared using organic or solvated metal cations.5,6 Metallocenes are strong donor molecules to give compounds that are generally prepared using organic or solvated metal cations.5,6 Metallocenes are strong donor molecules to give ionic fullerene systems.

Organometallic cations can introduce paramagnetic centers into the ionic fullerene systems.

In our previous work we studied coordination compounds of fullerene C\(_{60}\) with cobalt in zero oxidation state containing Ph\(_3\)P and diphosphine ligands (including 1,2-bis(diphenylphosphino)ethane, dppe) and in some cases benzonitrile.14–16 In this work we studied the interaction of fullerenes C\(_{60}\) and C\(_{70}\) with Co(dppe)\(_2\)Cl prepared by the reduction of Co\(^{II}\)(dppe)Cl\(_2\) with sodium fluorenone ketyl. Crystalline \((\text{Co(dppe)}_2\text{Cl})(\text{C}_{60})\) (1) and \((\text{Co(dppe)}_2\text{Cl})(\text{C}_{70})\cdot 0.5\text{C}_6\text{H}_4\text{Cl}_2\) (2) compounds were obtained together with the previously studied salt \((\text{Co(dppe)}_2^{\cdot -})(\text{C}_{60}^{\cdot -})\cdot 2\text{C}_6\text{H}_4\text{Cl}_2\).12 We present crystal structures, and optical and magnetic properties of these complexes. Compound 2 is a rare example of an ionic fullerene structure containing monomeric C\(_{70}^{\cdot -}\) radical anions while they form single-bonded \((\text{C}_{70}^{\cdot -})_2\) dimers17–19 in most of the anion radical salts.

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†Electronic supplementary information (ESI) available: IR spectra of 1 and 2. CCDC 1437134 and 1437135. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt04627k
Results and discussion

Synthesis

As summarized in Scheme 1, the first reduction potentials for fullerenes C_{60} and C_{70} are \(-0.44\) V and \(-0.41\) V, respectively, in dichloromethane vs. SCE. The second reduction wave is observed at \(-0.82\) V and \(-0.80\) V vs. SCE, respectively, in the same solvent.\(^{20}\) The \{Co^{II}(dppe)_{2}(CH_{3}CN)\}^{2+} cations can be reduced electrochemically to \{Co^{I}(dppe)_{2}\}^{2+} at \(-0.70\) V vs. Fe/C/Fe (\(-0.275\) V vs. SCE).\(^{21}\) Previously we used tetrakis(dimethylamino)ethylene (TDAE) as the reductant for Co^{II}(dppe)Br_{2} and C_{60}.\(^{12}\) TDAE with the first oxidation potential of \(E^{1/0} = \) \(-0.975\) V vs. SCE\(^{22}\) generates the Co^{I} species and C_{60}^{2-} in solution which co-crystallize to form the \{Co^{I}(dppe)_{2}(C_{60}^{2-})\} \cdot 2C_{6}H_{4}Cl_{2} salt.\(^{12}\) While the Co^{I}(dppe)_{2} cation has an odd \(S = 1\) or \(S = 0\) spin state, only the C_{60}^{2-} signal is observed in the EPR spectrum of this salt. Further reduction of Co^{I}(dppe)_{2}^{2+} to Co^{I}(dppe)_{2} by TDAE is not possible (Scheme 1) since the conversion takes place at a more negative redox potential of \(-1.56\) V vs. Fe/C/Fe (\(-1.135\) V vs. SCE).\(^{21}\) The Co^{I}(dppe)_{2} cation is also too weak a donor to reduce C_{60}^{2-} to C_{60}^{2-}.

Sodium fluorenone ketyl (fluorenone \(^{+}\)(Na\(^{-}\))) is a stronger reducing agent than TDAE (Scheme 1) with the first oxidation potential of about \(-1.30\) V vs. Ag/AgCl or (\(-1.255\) V vs. SCE).\(^{23}\) Therefore, this ketyl can also reduce Co^{II}(dppe)Cl_{2} to generate the Co^{I} species. Potentially it can also reduce Co^{II}(dppe)Cl_{2} to the Co^{0} species but such a redox process is hindered in non-polar \(\sigma\)-dichlorobenzene.

In this study, the formation of Co^{I} species was detected by the color change of the reaction mixture from the green color of Co^{II}(dppe)Cl_{2} to red during the reduction with sodium fluorenone ketyl. After the removal of unreacted sodium fluorenone ketyl by filtration, the generated Co^{I}(dppe)_{n} \(^{+}\) \((n = 1, 2)\) was treated with neutral fullerenes. Co^{I}(dppe)_{2}Cl is rather a strong donor and potentially it can reduce fullerenes providing the CT complexes composed of Co^{II}(dppe)_{2}^{2+} and C_{60}^{2-} or C_{70}^{2-} radical anions. While the main product of this reaction was \{Co^{II}(dppe)_{2}Cl\}(C_{60}) \((1)\), the \{Co^{II}(dppe)_{2}(C_{60}^{2-})\} \cdot 2C_{6}H_{4}Cl_{2} salt\(^{12}\) is also crystallized in 20\% yield. The \{Co(dppe)_{2}Cl\} \((C_{70})\) \cdot 0.5C_{6}H_{4}Cl_{2} \((2)\) complex crystallized exclusively with C_{70}.

Optical properties

The IR spectra of 1 and 2 are listed in Table S1\(^{\dagger}\) and are shown in Fig. 1S and 2S.\(^{\dagger}\) The spectra practically seem to be the superposition of the absorption bands of Co(dppe)_{2}Cl and fullerene anions C_{60}^{2-} or C_{70}^{2-}. Neutral fullerene C_{60} shows four \(F_{1u}\) mode IR bands at 527, 576, 1183, and 1429 cm\(^{-1}\) (denoted as \(F_{1u}(1)\) to \(F_{1u}(4)\), respectively).\(^{24,25}\) While other bands exhibit only a few cm\(^{-1}\) shifts, the \(F_{1u}(4)\) mode shows a 37 cm\(^{-1}\) red shift when C_{60} is charged \(-1\). The strong absorption band observed at 1393 cm\(^{-1}\) for 1 unambiguously indicates the formation of C_{60}^{2-}. The coexistence of partially reduced or neutral C_{60} cannot be confirmed from the IR spectrum since Co(dppe)_{2}Cl has intense absorption bands at 1433 and 530 cm\(^{-1}\) which coincide with those of neutral C_{60}. A similar situation is observed for complex 2 containing C_{70} (Table S1\(^{\dagger}\)).

The UV-visible-NIR spectra of 1 and 2 are shown in Fig. 1. The absorption bands in the spectrum of 1 at 38000, 29700 cm\(^{-1}\) (262, 334 nm) and the weaker band at 16 860 cm\(^{-1}\) (612 nm) can be attributed to C_{60} whereas the bands in the NIR range at 10 650 and 9240 cm\(^{-1}\) (948, 1087 nm) (Fig. 1a) show the presence of C_{60}^{2-}.\(^{5,6}\) The broad low-energy band of relatively weak intensity at about 7660 cm\(^{-1}\) (1300 nm) (Fig. 1a) can be ascribed to the CT transition between fullerenes or the Co(dppe)_{2}Cl and fullerene species. Similarly, absorption bands in the spectrum of 2 at 26000 and 20 840 cm\(^{-1}\) (382 and 480 nm) are ascribed to C_{70}. The broad absorption band in the NIR range can be reproduced by two Gaussian curves with maxima at about 9900 and 7500 cm\(^{-1}\) (1010 and 1330 nm, Fig. 1b and 2). The position of the latter band is close to that in the solution spectrum of monomeric C_{70}^{2-}.\(^{5,6,26}\) It should be noted that generally C_{70} mononaions form singly bonded \((C_{70})_{2}\) dimers in solids to show two bands in the NIR range at about 11 360 and 8200 cm\(^{-1}\) (880 and 1220 nm, Fig. 2).\(^{17,19}\) The strong shift of the \((C_{70})_{3}\) band at 880 nm to 1010 nm in the spectrum of 2 proves the failure of dimer formation in 2. So far, monomeric C_{70}^{2-} are preserved only in the \((Ph_{4}P)_{2}(C_{70})^{-}((I))\) salt due to the long distances between fullerenes.\(^{27}\) The broad band at about 9900 cm\(^{-1}\) (1010 nm) can be attributed to the CT between fullerenes or the Co(dppe)_{2}Cl and the fullerene species. Low energy CT bands (ca. 2000–5000 cm\(^{-1}\)) which correspond to the Drude type reflectivity spectra characteristic of metals are not observed in the spectra of both 1 and 2.

![Fig. 1 Spectra of 1 (a) and 2 (b) in the UV-visible-NIR range measured at room temperature using KBr pellets prepared under anaerobic conditions.](image-url)

**Scheme 1** Redox potentials of the components used in the synthesis of Co(dppe)\(_{2}\)-fullerene complexes. All potentials are given vs. SCE.
Crystal structures

\{\text{Co(dppe)}_2\text{Cl}\}(\text{C}_60)\ \text{(1)} \text{ contains closely packed zigzag fullerene chains arranged along the } c \text{ axis with equal interfullerene center-to-center (ctc) distances of } 9.97 \text{ Å. This distance is noticeably shorter than the van der Waals (vdW) diameter of C}_{60} (10.18 \text{ Å}) \text{ and multiple vdW } C\cdots C \text{ contacts are formed between fullerenes (shown by green dashed lines in Fig. 3a). Fullerene chains are isolated (Fig. 3b), and the shortest ctc interfullerene distance between the neighboring chains is 12.53 Å. Each } \text{Co(dppe)}_2\text{Cl unit is surrounded by four } C_{60} \text{ cages (Fig. 3c). Nearly spherical } C_{60} \text{ is inserted into the cavities formed by four phenyl substituents of } \text{Co(dppe)}_2\text{Cl, and multiple vdW } C\cdots H(Co(dppe)_2Cl)\cdots C(C_{60}) \text{ contacts are formed. One of the four surrounding fullerenes forms short } Cl(\text{Co(dppe)}_2\text{Cl})\cdots C(C_{60}) \text{ contacts of the } 2.998\text{–}3.107 \text{ Å length. The shortest distances (5.22\text{–}5.41 \text{ Å}) between cobalt and the } C_{60} \text{ carbon atoms are attained with the fullerene closest to the chloride anion of } \text{Co(dppe)}_2\text{Cl.}

Fullerenes C_{70} form closely packed double chains arranged along the } a \text{ axis in } \{\text{Co(dppe)}_2\text{Cl}\}(\text{C}_{70})\cdot 0.5C_6H_4Cl_2 \text{ (2) (Fig. 3d). The longer axis of C}_{70} \text{ is directed along this axis, and the ctc interfullerene distance is 10.81 Å in this direction. The ctc interfullerene distance in the double chains along the } b \text{ axis is } 10.18 \text{ Å. As a result, multiple short vdW } C\cdots C \text{ contacts are formed between fullerenes (shown with green dashed lines in Fig. 4a). Double fullerene chains are completely isolated to give the ctc interfullerene distances among the neighboring double chains longer than } 14 \text{ Å (Fig. 4b). Each } \text{Co(dppe)}_2\text{Cl unit is surrounded by four } C_{70} \text{ cages in 2 (Fig. 4c). In this case phenyl substituents cannot form a suitable cavity for a larger } C_{70} \text{ ellipsoid, and it is positioned asymmetrically to } \text{Co(dppe)}_2\text{Cl (Fig. 4c). There are no short } Cl(\text{Co(dppe)}_2\text{Cl})\cdots C(C_{70}) \text{ contacts in 2 unlike the crystal structure of 1. The shortest } Co\cdots C(C_{70}) \text{ distances are 5.94\text{–}6.70 \text{ Å.}

The arrangement of ligands around cobalt atoms in the \text{Co(dppe)}_2\text{Cl units is similar in 1 and 2. However, these units have different bond lengths at the cobalt atoms. The cobalt atoms are located in the pyramidal environment in both the units formed by four phosphorus atoms and one chloride anion. The Co atoms are not located strictly in the plane of four phosphorus atoms but move out of this plane by 0.110 \text{ and } 0.124 \text{ Å towards chloride anion in 1 and 2, respectively. The dimension of pyramidal coordination is informative to evaluate the charge on Co. As listed in Table 1, the average of Co–P length is increased according to the charge on Co (see, 16, 3–5).}

The value of 2.2725(8) Å for 2 proves that Co is oxidized in this complex to almost +2, which corresponds well to a similar Co–Cl length to that of #3. On the contrary, the average Co–P length in 1 is shortened compared to those in Co^{II} materials.

Compared with that in #0, the Co in 1 is regarded not to be oxidized fully to +2. This evaluation corresponds well to the optical spectra and magnetic data for 1.

Magnetic properties

Magnetic properties of 1 and 2 were studied by SQUID and EPR techniques. Effective magnetic moments of 1 and 2 are 1.98 and 2.27μ_B at 300 K, respectively. These values are inter-
mediate between those characteristic of the systems of one and two non-interacting $S = 1/2$ spins per formula unit (1.73 and 2.45 $\mu_B$, respectively). In the case of 2, the magnetic moment is closer to 2.45 $\mu_B$ than that of 1. We suppose that paramagnetic CoII(dppe)$_2$Cl$^+$ cations and C$_{60}^-$ or C$_{70}^-$ radical anions with the $S = 1/2$ spin state are formed in both complexes due to CT from Co(dppe)$_2$Cl to fullerenes. Since the magnetic moment of 2.45 $\mu_B$ is expected in the fully charge-transferred {CoII(dppe)$_2$Cl}$(\text{fullerene})^-$ state, the observed lower magnetic moments are most probably due to the coexistence of diamagnetic {CoI(dppe)$_2$Cl}$^0$(fullerene)$^0$ with the total magnetic moments of $S = 0$. Moreover, magnetic moments are not constant at high temperature and increases above 220 K for 1 and 140 K for 2 (Fig. 5a and b). Such behavior can be explained by the increase of the degree of CT from Co(dppe)$_2$Cl to fullerenes with temperature. The low-temperature part can be approximated well by the Curie–Weiss expression with Weiss temperatures of only $-2$ and $-3.5$ K for 1 and 2, respectively (Fig. 5c and d). Thus, in spite of close packing of fullerenes in 1 and 2, only weak antiferromagnetic coupling of spins and no long range ordering are observed in both complexes. The presence of neutral diamagnetic components and disordered fullerenes can interrupt the phase transition. Incomplete CT to fullerenes can also be the reason for the absence of fullerene dimerization in spite of their close packing in a crystal. Particularly, complex 2 should be noted since the formation of stable singly bonded (C$_{70}^-$)$_2$ dimers is observed in almost all the ionic compounds of C$_{70}^-$.$^{17-19}$ The similar exceptional absence of dimerization was found for C$_{60}$ complexes with partial CT states on average.$^{20}$

Complex 1 manifests an intense asymmetric EPR signal at room temperature which can be fitted well by three components with $g_1 = 2.0968$ (the linewidth ($\Delta H$) of 15.51 mT),
Higher values in comparison with that of CoII(dppe)Br2. The starting CoI has a tetrahedral geometry while the Co II(dppe)2Cl+ cations have the pyramidal environment for the cobalt atoms. Essential modification of the cobalt environment in the formation of CoII(dppe)2Cl+ can affect the EPR signal by shifting g-factors to higher values in comparison with that of CoII(dppe)Br2. The signals with a g-factor closer to that of C60− are also observed (g1 = 2.0488 and g2 = 2.0085) together with the signals characteristic of CoII. These signals could be ascribed to both CoII(dppe)2Cl+ and C60− species having exchange interaction. They are strongly narrowed with the temperature decrease (Fig. 6c) and grow in intensity with the temperature increase above 220 K. We attribute such behavior to the increase of the CT degree from Co(dppe)2Cl to C60. The component with g1 = 2.0980 splits into two components below 40 K positioned at g1 = 2.0979 and 2.1501. Both components shift to higher g-factors with the temperature decrease (Fig. 6b).

Complex 2 shows an intense EPR signal at room temperature which can be fitted by three Lorentzian lines with g1 = 2.3235 (ΔH = 5.62 mT), g2 = 2.2649 (ΔH = 9.20 mT), and g3 = 2.1428 (ΔH = 24.84 mT) (Fig. 7). The broad g1-component splits into two lines below 220 K which are positioned at g1 = 2.1829 (ΔH = 13.86 mT) and 2.0711 (ΔH = 25.64 mT) at 220 K. Spectrum of 2 contains also weak narrow signal with g = 2.0021 (ΔH = 0.28 mT) (Fig. 7a) which can appear due to air oxidation of fullerene anions. It is seen that the EPR signal in 2 is broader and has essentially higher g-factors of the lines in comparison with those of 1. We can suppose that lines in the EPR spectrum of 2 with lower g-factors of 2.18 and 2.07 have essential contribution from C70−. It is known that the C70− radical anions in (Ph4P)2(C70−)2(I−) show a broad EPR signal with a g-factor of 2.0047 (ΔH = 60 mT) at 300 K.27 Therefore, the lines in the spectrum of 2 originating from both CoII(dppe)2Cl+ and C70− are essentially broader and shifted to higher g-factors in comparison with those of 1. Lines with lower g-factors (g = 2.18 and 2.07) slightly grow in intensity with the temperature increase above 150 K and that can also be explained by the increase of the CT degree from CoII(dppe)2Cl to C70−.

**Experimental**

**Materials**

C60 of 99.9% purity and C70 of 99% purity were obtained from MTR Ltd and used without further purification. CoII(dppe)Cl2 (98%) was purchased from Aldrich. Sodium fluorenone ketyl
was obtained as described.\textsuperscript{32} Solvents were purified under an argon atmosphere and degassed. \textit{o}-Dichlorobenzene (C\textsubscript{6}H\textsubscript{4}Cl\textsubscript{2}) was distilled over CaH\textsubscript{2} under reduced pressure and hexane was distilled over Na/benzophenone. All manipulations for the syntheses of 1 and 2 were carried out in an MBraun 150B-G glove box with a controlled argon atmosphere and the content of H\textsubscript{2}O and O\textsubscript{2} less than 1 ppm. The solvents and crystals were stored in the glove box. Polycrystalline samples of 1 and 2 were placed in 2 mm quartz tubes under anaerobic conditions for EPR and SQUID measurements and sealed under 10\textsuperscript{−5} torr pressure. KBr pellets for IR- and UV-visible-NIR measurements were prepared in the glove box.

**Synthesis**

Crystals of 1 and 2 were obtained by a diffusion technique. A reaction mixture was filtered into a 1.8-cm-diameter, 50 mL glass tube with a ground glass plug, and then 30 mL of hexane was layered over the solution. Slow mixing of the solutions resulted in precipitation of crystals over 1 month. The solvent was then decanted from the crystals, and they were washed with hexane. The compositions of the obtained salts were determined from X-ray diffraction analysis on a single crystal. Due to the high air sensitivity of 1 and 2, elemental analysis could not be carried out to determine the composition because the salts reacted with oxygen in air before the quantitative oxidation procedure.

The crystals of \{Co(dppe)\textsubscript{2}Cl\}(C\textsubscript{6}0\textsubscript{60})\textsubscript{2} (1) and \{Co(dppe)\textsubscript{2}Cl\}(C\textsubscript{70})\textsubscript{2} (2) were obtained by the following procedure. The reduction of green CoII(dppe)Cl\textsubscript{2} (22 mg, 0.042 mmol) in 16 ml of C\textsubscript{6}H\textsubscript{4}HCl\textsubscript{2} with sodium fluorenone ketyl (20 mg, 0.098 mmol) for 2 hours at 100 °C yielded a clear red solution. The solution was cooled down to room temperature and filtered into a flask containing fullerene C\textsubscript{6}0 (30 mg, 0.042 mmol) for preparation of 1 and fullerene C\textsubscript{70} (35 mg, 0.042 mmol) for preparation of 2. Fullerenes were dissolved in the obtained solution over 4 hours at 80 °C to produce violet-red and red solutions, respectively. After cooling down to room temperature the solutions were filtered into the tube for diffusion. The crystals of \{Co(dppe)\textsubscript{2}Cl\}(C\textsubscript{6}0\textsubscript{60})\textsubscript{2} (1) were obtained as black plates in 26% yield together with black elongated parallelepipeds of the previously reported salt \{Co(dppe)\textsubscript{2}Cl\}(C\textsubscript{6}0\textsubscript{60})\textsubscript{2} (yield is 20%) which was identified by X-ray diffraction on several parallelepipeds-shaped single crystals. The crystals of two phases have different shapes and were separated under a microscope in the glove box. The purity of 1 was supported by the absence of the line at g = 1.9986 (\Delta H = 4.57 mT) characteristic of \{Co(dppe)\textsubscript{2}Cl\}(C\textsubscript{6}0\textsubscript{60})\textsubscript{2} (yield is 20%). The crystals of \{Co(dppe)\textsubscript{2}Cl\}(C\textsubscript{70})\textsubscript{2} (2) were obtained as black plates in 42% yield. Testing of several crystals from the synthesis shows the presence of only one phase in this synthesis.

**General**

UV-visible-NIR spectra were recorded using KBr pellets on a PerkinElmer Lambda 1050 spectrometer in the 250–2500 nm range. FT-IR spectra were obtained using KBr pellets with a Perkin-Elmer Spectrum 400 spectrometer (400–7800 cm\textsuperscript{-1}). EPR spectra were recorded for polycrystalline samples of 1 and 2 with a JEOL JES-TE 200 X-band ESR spectrometer equipped with a JEOL ES-CT470 cryostat working between room and liquid helium temperatures. A Quantum Design MPMS-XL SQUID magnetometer was used to measure the static magnetic susceptibility of 1 and 2 at 100 mT magnetic field under cooling and heating conditions in the 300–1.9 K range. The sample holder contribution and core temperature independent diamagnetic susceptibility (\chi_{d}) were subtracted from the experimental values. The X\textsubscript{A} values were estimated by the extrapolation of the data in the high-temperature range by fitting the data with the following expression: \chi_{A} = C/(T - \Theta) + X\textsubscript{A}, where C is the Curie constant and \Theta is the Weiss temperature. The effective magnetic moment (\mu_{eff}) was calculated with the formula \mu_{eff} = (8Z_{M}T)^{1/2}

**Crystal structure determination**

The intensity data for 1 and 2 were collected on an IPDS (Stoe) diffractometer with graphite monochromated Mo-K\textsubscript{α} radiation (\lambda = 0.71073 Å). The structures were solved by a direct method and refined by a full-matrix least-squares method against F\textsuperscript{2} using SHELXL 2014\textsuperscript{7,33} All non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms were included into refinement in a riding model. See the ESI\textsuperscript{†} for crystallographic data in CIF format.

**Conclusions**

The interaction of the Co\textsuperscript{I} species generated by the reduction of Co\textsuperscript{II}dppeCl\textsubscript{2} allows the preparation of CT complexes \{Co(dppe)\textsubscript{2}Cl\}(C\textsubscript{6}0\textsubscript{60})\textsubscript{2} and \{Co(dppe)\textsubscript{2}Cl\}(C\textsubscript{70})\textsubscript{2}·0.5C\textsubscript{6}H\textsubscript{4}HCl\textsubscript{2}. Both complexes contain the C\textsubscript{6}0\textsubscript{60}\textsuperscript{−} or C\textsubscript{70}\textsuperscript{−} radical anions and the Co\textsuperscript{II}(dppe)\textsubscript{2}Cl\textsuperscript{+} cations formed as a result of CT from Co\textsuperscript{II}(dppe)Cl\textsubscript{2} to fullerenes. CT becomes possible due to the
strong donor properties of Co(dppe)Cl which are enough to produce fullerene$^-$ radical anions. However, most probably CT is not complete and diamagnetic{Co(dppe)$_2$Cl}$^0$ and neutral fullerenes are also preserved in the samples. As a result, in spite of the close packing of fullerenes in the chains only weak magnetic coupling of spins is observed and fullerenes are not dimerized in both complexes. The absence of dimerization allows for the first time to observe the solid state optical spectrum of monomeric C$_{70}^-$ radical anions and to determine their molecular structure. It is also seen that organometalllic compounds with strong donor properties can be promising components to design fullerene complexes with partial CT.

Acknowledgements

The work was supported by the Russian Science Foundation (project no. 14-13-00028) and by JSPS KAKENHI Grant Numbers 23225005 and 26288035.

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