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Effect of the Co–C(C_{60}^-) bond formation on magnetic properties of the ionic complex $\{\text{cryptand}[2,2,2]\cdot(\text{Na}^+)\}\cdot\{\text{Co}^{\text{II}}\text{TPP}\cdot(\text{C}_{60}^-)\}\cdot(\text{C}_6\text{H}_4\text{Cl}_2)_2$†

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A new ionic complex $\{\text{cryptand}[2,2,2]\cdot(\text{Na}^+)\}\cdot\{\text{Co}^{\text{II}}\text{TPP}\cdot(\text{C}_{60}^-)\}\cdot(\text{C}_6\text{H}_4\text{Cl}_2)_2$ has been obtained as single crystals by a diffusion technique. It involves coordination $\{\text{Co}^{\text{II}}\text{TPP}\cdot(\text{C}_{60}^-)\}$ units and bulky $\{\text{cryptand}[2,2,2]\cdot(\text{Na}^+)\}$ cations. The Co–C(C_{60}^-) coordination bond is short (2.262(2) Å at 100 K) which provides ordering in the C_{60}^- anions. This is the first ordered structure of $\{\text{Co}^{\text{II}}\text{TPP}\cdot(\text{C}_{60}^-)\}$. The coordination bonds weaken upon heating to be 2.316(4) Å at 250 K. As a result, the C_{60}^- anions begin to rotate at 250 K about the Co–C bond between two orientations. The complex is diamagnetic from 4 up to 320 K. The Co–C bonds dissociate above 320 K only to form unbound paramagnetic Co^{II}TPP and $\text{C}_{60}^{\bullet-}$ species. The process is accompanied by the reversible increase in magnetic susceptibility of the complex and the appearance of a new broad EPR signal with $g = 2.1187$ and a linewidth of ~120 mT (350 K). The signal was attributed to both paramagnetic Co^{II}TPP and $\text{C}_{60}^{\bullet-}$, which showed strong exchange interaction.

Introduction

Fullerenes form a variety of molecular and ionic complexes with metalloporphyrins.[1–6] Some metalloporphyrins can cocrystallize with endometallofullerenes, higher fullerenes and fullerene derivatives.[7–9] In many cases the metal–fullerene interaction is responsible for the ordering of fullerenes and allows one to determine molecular structures of new fullerenes. Among different porphyrins, cobalt(II) porphyrins form short M$\cdots$C contacts in the 2.58–2.70 Å range.[1,4,10–12] The study of ionic complexes of cobalt(II) porphyrins with fullerene radical anions showed them to be essentially stronger ligands than neutral fullerenes to form shorter Co–C contacts in the 2.29–2.32 Å range.[10,13,14] The coordination between cobalt(II) porphyrins and fullerene radical anions is realized by σ-type. Similar coordination mode was found in alkylcobalamines with the essentially shorter Co–C bond length of 1.99–2.03 Å.[15] Both electrons from cobalt(II) porphyrin and the fullerene radical anion is involved in the formation of the coordination bond. As a result, the $\{\text{Co}^{\text{II}}\text{porphyrin}\cdot(\text{C}_{60}^-)\}$ units are diamagnetic. Since these bonds are rather weak, their dissociation produces two paramagnetic species (Co^{II}porphyrin and $\text{C}_{60}^{\bullet-}$). Thus, the dynamics of the formation of the Co–C(C_{60}^-) bonds can be studied. The coordination of fullerene radical anions to cobalt(II) porphyrins was found in several complexes with cobalt(II) tetraphenylporphyrin (Co^{II}TPP): $[\text{Cr}^{\text{I}}(\text{C}_6\text{H}_6)_2^{\bullet+}]_{1.7}\cdot\{\text{Co}^{\text{II}}\text{TPP}\cdot(\text{C}_{60}^-)\}_2\cdot(\text{C}_6\text{H}_4\text{Cl}_2)_{3.3}$, $[\text{Cr}^{\text{I}}(\text{C}_6\text{H}_6)_2^{\bullet+}]_2\cdot\{\text{Co}^{\text{II}}\text{TPP}\cdot\text{C}_{60}(\text{CN})_2^-)\}\cdot(\text{C}_{60}(\text{CN})_2^{\bullet-})\cdot(\text{C}_6\text{H}_4\text{Cl}_2)_3$[10] and cobalt(II) octaethylporphyrin (Co^{II}OEP): $(\text{TMP}^+)\cdot\{\text{Co}^{\text{II}}\text{OEP}\cdot(\text{C}_{60}^-)\}\cdot(\text{C}_6\text{H}_5\text{CN})_{0.75}\cdot(\text{C}_6\text{H}_4\text{Cl}_2)_{0.25}$, $\{(\text{MDABCO}^+)\cdot\text{Co}^{\text{II}}\text{OEP}\cdot(\text{C}_{60}^-)\}\cdot(\text{C}_6\text{H}_5\text{CN})_{0.67}\cdot(\text{C}_6\text{H}_4\text{Cl}_2)_{0.33}$[14] ($\text{Cr}(\text{C}_6\text{H}_6)_2$: bis(benzene)-chromium; TMP^+: tetramethylphosphonium cation; MDABCO^+: the cation of *N*-methyldiazabicyclooctane). In the latter case the MDABCO^+ cations also coordinate to Co^{II}OEP to form six-coordinated cobalt(II) centers in the $(\text{MDABCO}^+)\cdot\text{Co}^{\text{II}}\text{OEP}\cdot(\text{C}_{60}^-)$ units. The Co–C(C_{60}^-) bonds are destabilized and dissociate in the 50–250 K range, whereas the complex transforms from a diamagnetic to a paramagnetic one. However, dissociation temperatures are still unknown for the individual $\{\text{Co}^{\text{II}}\text{porphyrin}\cdot(\text{C}_{60}^-)\}$ coordination units. There is also the problem of disorder of fullerene anions due to their rotation about the Co–C bonds which prevents studying the precise molecular structure of the $\{\text{Co}^{\text{II}}\text{porphyrin}\cdot(\text{C}_{60}^-)\}$ units.

In this work we obtained a novel ionic complex of cobalt(II) tetraphenylporphyrin with C_{60} stabilized by bulky $\{\text{cryptand}[2,2,2]\cdot(\text{Na}^+)\}$ cations. The crystal structure of the complex was solved at 100 and 250 K. Fullerene anions coordinate to Co^{II}TPP to form σ-bonded $\{\text{Co}^{\text{II}}\text{TPP}\cdot(\text{C}_{60}^-)\}$ units with short Co–C bonds. The increase in the Co–C bond length and the transition of fullerene anions from an ordered to a disordered state upon heating was observed. Magnetic measurements carried out from liquid helium temperatures up to 360 K (EPR) and 400 K (SQUID). The dissociation temperature of the $\{\text{Co}^{\text{II}}\text{TPP}\cdot(\text{C}_{60}^-)\}$ coordination units was determined. It was shown that $\{\text{Co}^{\text{II}}\text{TPP}\cdot(\text{C}_{60}^-)\}$ coordination units dissociate to unbound paramagnetic Co^{II}TPP and $\text{C}_{60}^{\bullet-}$ species.

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Results and discussion

The crystals of the complex were obtained by diffusion technique as prisms with characteristic for porphyrins blue lustre. The composition of the complex was determined from X-ray diffraction on a single crystal: $\{\text{cryptand[2,2,2]}\cdot(\text{Na}^+)\}\cdot\{\text{Co}^{\text{II}}\text{TPP}\cdot(\text{C}_{60}^-)\}\cdot(\text{C}_6\text{H}_4\text{Cl}_2)_2$ (**1**). Several crystals from the synthesis were found to have the same unit cell parameters.

The complex contains crystallographically independent C_{60}, Co^{II}TPP, $\{\text{cryptand[2,2,2]}\cdot(\text{Na}^+)\}$ and two solvent molecules. At 100 K all crystallographically independent units are ordered except one solvent molecule which is disordered between two orientations. The main building block of **1** is the $\{\text{cryptand[2,2,2]}\cdot(\text{Na}^+)\}\cdot\{\text{Co}^{\text{II}}\text{TPP}\cdot(\text{C}_{60}^-)\}$ unit (Fig. 1(a)). The Co atom has one short (2.262(2) Å) $\text{Co}\cdots\text{C}(\text{C}_{60}^-)$ contact which is evidence of a σ-type coordination of C_{60}^- to Co^{II}TPP. The $\text{Co}\cdots\text{C}$ contacts with other carbon atoms of C_{60}^- are longer than 2.9 Å. The C–C bonds closest to the coordinated carbon atom have a length of 1.431(2) Å for the C(6)–C(6) bond and 1.488(2) and 1.449(2) Å for the C(6)–C(5) bonds. The cobalt atom displaces 0.131(2) Å out of the plane of four nitrogen atoms of the porphyrin macrocycle towards C_{60}^-. The average $\text{Co}\cdots\text{N(TPP)}$ distance is 1.986(2) Å. The $\text{Co}\cdots\text{C}$ bond in **1** is noticeably shorter and the displacement of the Co atoms from the plane of four nitrogen atoms is greater than those observed in $(\text{Cr}^{\text{I}}(\text{C}_6\text{H}_6)_2^{\bullet+})_{1.7}\cdot[(\text{Co}^{\text{II}}\text{TPP}\cdot\text{C}_{60})_2]^{1.7-}\cdot(\text{C}_6\text{H}_4\text{Cl}_2)_{3.3}$ (**2**); 2.29–2.32 Å and 0.091–0.096 Å, respectively.[10] One of possible reasons for this is that the negative charge on C_{60} in **2** (formal charge is −0.85)[10] is smaller than that observed in **1** (formal charge is −1). Since neutral fullerenes are weaker ligands than negatively charged fullerenes, the decrease of negative charge on C_{60} can weaken the Co–C bonds. Another factor affecting the length of the $\text{Co–C}(\text{C}_{60}^-)$ bonds is the coordination of the *N*-containing cations to the cobalt(II) porphyrin as was found in $\{(\text{MDABCO}^+)\cdot\text{Co}^{\text{II}}\text{OEP}\cdot(\text{C}_{60}^-)\}$. The MDABCO^+ cation is located in the opposite side of the porphyrin macrocycle relative to C_{60}^- and such coordination elongates the $\text{Co–C}(\text{C}_{60}^-)$ bonds to 2.51 Å.[14]

Bulky $\{\text{cryptand[2,2,2]}\cdot(\text{Na}^+)\}$ cations are located in the opposite side of the porphyrin macrocycle relative to C_{60}^- (Fig. 1(a)). The shortest $\text{C,N(cryptand)}\cdots\text{Co}$ distances are longer than 4.5 Å. Since $\{\text{cryptand[2,2,2]}\cdot(\text{Na}^+)\}$ cannot coordinate to Co^{II}TPP, it does not affect $\text{Co–C}(\text{C}_{60}^-)$ bonding. In general, the packing of the complex can be described as zigzag chains of $\{\text{cryptand[2,2,2]}\cdot(\text{Na}^+)\}\cdot\{\text{Co}^{\text{II}}\text{TPP}\cdot(\text{C}_{60}^-)\}$ units (Fig. 1(b)) arranged along the *b* axis (Fig. 1(b)). Fullerenes are isolated in the chains by the $\{\text{cryptand[2,2,2]}\cdot(\text{Na}^+)\}$ cations and solvent molecules. However, they form multiple C, H van der Waals (vdW) contacts with the cations and phenyl groups of Co^{II}TPP. In total three cations surround each C_{60}^- and form vdW contacts with it.

A temperature increase up to 250 K induces disorder in the crystal structure of **1**. Both $\text{C}_6\text{H}_4\text{Cl}_2$ molecules are disordered between two orientations. Fullerene anions begin to rotate by 140° about the $\text{Co–C}(\text{C}_{60}^-)$ bond between two orientations. In such disorder only one carbon atom involved in the Co–C bond is ordered, whereas all other carbon atoms are disordered. One of the reasons for rotation can be the weakening of the $\text{Co–C}(\text{C}_{60}^-)$ bond which elongates to 2.316(4) Å. The displacement of the Co atom from the plane of four nitrogen atoms decreases to 0.125(2) Å. The C–C bonds closest to the coordinated carbon atom are nearly the same length for the C(6)–C(6) bond (1.438(2) Å) and become closer to each other for the C(6)–C(5) bonds (1.463(2) and 1.456(2) Å).

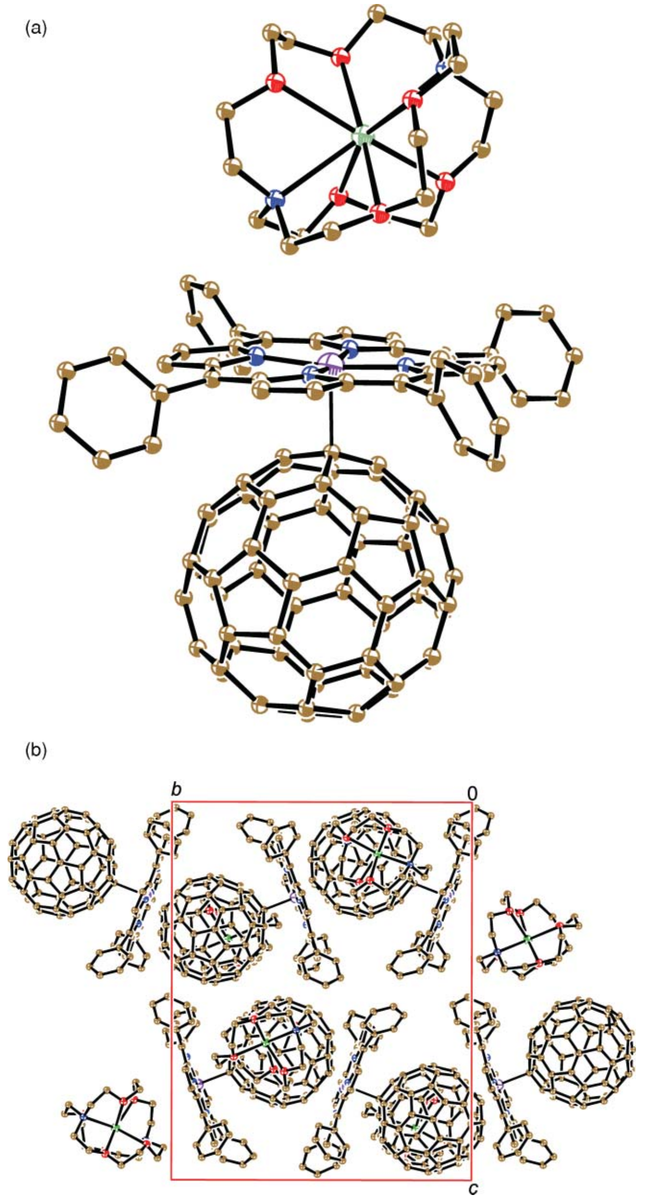

Fig. 1 Crystal structure of **1** at 100 K at 25% probability level: (a) the building block of **1** contains the coordination $\{\text{Co}^{\text{II}}\text{TPP}\cdot(\text{C}_{60}^-)\}$ and $\{\text{cryptand[2,2,2]}\cdot(\text{Na}^+)\}$ units. (b) Fragment of the unit cell of **1** is viewed along the *a* axis. Solvent $\text{C}_6\text{H}_4\text{Cl}_2$ molecules are not depicted for clarity.

The IR spectrum of **1** was measured in KBr pellets under anaerobic conditions (see ESI†). Since the ratio between the cations and C_{60} is exactly 1 : 1, the formal charge on C_{60} is −1. The $F_{1u}(4)$ mode of C_{60} is most sensitive in its charged state.[16] The IR spectrum manifests a split band of this mode at 1405 and 1399 cm^{-1}. The position of this mode is shifted relative to neutral C_{60} (1429 cm^{-1}) and becomes closer to the position in the spectra of fully ionic complexes (1386–1396 cm^{-1})[17–19] indicating a negative charge on C_{60}. However, due to that the shift is slightly smaller than that in the spectra of fully ionic complexes; the real charge on C_{60} can also be smaller than –1, probably due to the redistribution of electron density from C_{60}^- to $Co^{II}TPP$ in the coordination $\{Co^{II}TPP\cdot(C_{60}^-)\}$ units. However, the total charge on these units must be –1 to provide electroneutrality of the complex. The UV-visible-NIR spectrum of **1** is shown in Fig. 2. The bands at 262 and 338 nm were attributed to C_{60}, whereas the bands at 422 and 532 nm were attributed to the Soret and Q-bands of $Co^{II}TPP$, respectively. In the spectrum of individual $Co^{II}TPP$ the positions of these bands are at 421, 536, and 617 nm. Therefore, the bands of the metalloporphyrin only slightly shift at the formation of the complex despite the coordination of C_{60}^-. Two bands were found at 1082 and 1280 nm in the NIR range. The first band was attributed to intramolecular transitions in the C_{60}^- anions. The second band was observed in the spectra of the complexes comprising the coordination Co–C bonds.[10,14] Therefore, this band can be ascribed to charge transfer in the $\{Co^{II}porphyrin\cdot(C_{60}^-)\}$ units as a result of the absorption of light quantum.

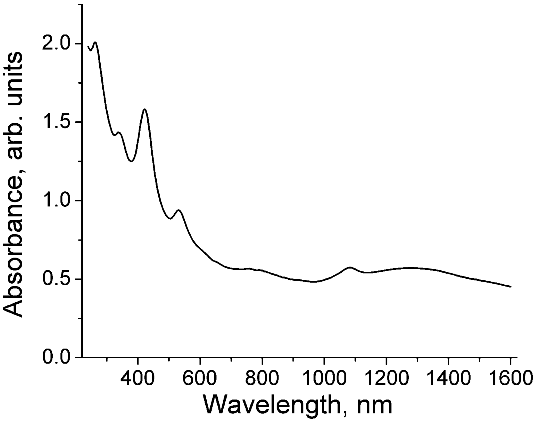

Fig. 2 UV-visible-NIR spectrum of **1** in KBr pellet in the 1600–240 nm range.

Magnetic properties of **1** were studied by EPR and SQUID techniques. One weak single line with $g = 2.0000$ and linewidth $(\Delta H) = 6.4$ mT is observed in the EPR spectrum below room temperature (RT). The signal, which is observed down to 4 K, shows paramagnetic temperature dependence and strongly narrows when the temperature decreases. Such behavior allows it to be attributed to the admixture of the $C_{60}^{\bullet -}$ radical anions. According to SQUID measurements the complex is diamagnetic. At low temperatures Curie impurities (most probably originating from the traces of $C_{60}^{\bullet -}$) were estimated to be only about 3.4% of the total amount of C_{60}. A new broad signal appears in the EPR spectrum above 320 K. The signal grows with temperature. At 350 K, $g = 2.1187$ and $\Delta H = 120$ mT (Fig. 3(a)). Since the signal has an intermediate g-factor value between those characteristic of $Co^{II}TPP$ ($g = 2.3$–2.5) and $C_{60}^{\bullet -}$ ($g = 2$), it can be attributed to both paramagnetic $Co^{II}TPP$ and $C_{60}^{\bullet -}$ species, which have strong exchange interaction. Previously, a similar signal with $g = 2.1188$ and $\Delta H = 52$ mT was detected at the dissociation of the coordination Co–C bonds in the $\{(MDABCO^+)\cdot Co^{II}OEP\cdot(C_{60}^-)\}$ units.[14]

Diamagnetism of the complex is manifested up to 320 K. The reversible increase in magnetic susceptibility is observed only above 320 K (Fig. 3(b)). Since a broad EPR signal appears at the same temperature, both processes can be attributed to the dissociation of the $\{Co^{II}TPP\cdot(C_{60}^-)\}$ units and the formation of paramagnetic $Co^{II}TPP$ and $C_{60}^{\bullet -}$ species. They make a positive contribution to magnetic susceptibility and manifest a new EPR signal. Most probably, the diamagnetic–paramagnetic transition is rather broad in **1** (as in $\{(MDABCO^+)\cdot Co^{II}OEP\cdot(C_{60}^-)\}$)[14] since it is not finished even at 400 K. Further heating of the compound is impossible because of the loss of crystallinity probably as a result of the elimination of solvent molecules. Nevertheless, heating only up to 400 K provides a completely reversible diamagnetic–paramagnetic transition.

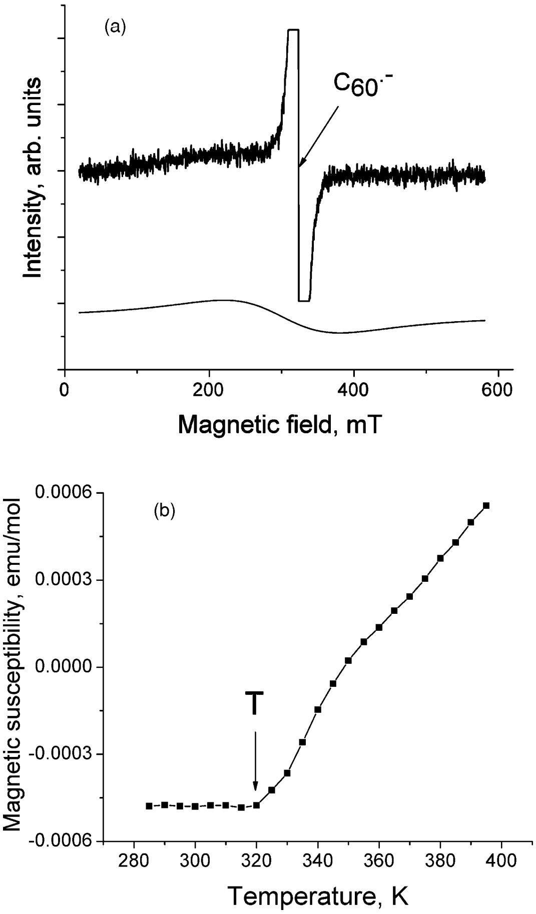

Fig. 3 (a) EPR spectrum of **1** at 350 K. Simulation of the broad signal appearing above 320 K by one Lorenz line is shown below. (b) Temperature dependence of molar magnetic susceptibility of **1** above 285 K. The behavior is reversible. *T* is temperature at the beginning of the dissociation of $\{Co^{II}TPP\cdot(C_{60}^-)\}$ units.

Coordination of $C_{60}^{\bullet -}$ to $Co^{II}TPP$ is similar to dimerization of $C_{60}^{\bullet -}$. However, $(C_{60}^-)_2$ dimers, bonded by one C–C bond, are noticeably less stable (the beginning of dissociation is from 130 to 280 K)[18,20–27] than the coordination $\{Co^{II}TPP\cdot(C_{60}^-)\}$ units (the beginning of dissociation is above 320 K), though the covalent C–C bonds in the dimers (1.58–1.60 Å)[21,22] are noticeably shorter than the Co–C bonds (2.26–2.32 Å). Destabilization of the $(C_{60}^-)_2$ dimers can be a result of the repulsion of negative charges of C_{60}^-, while no electrostatic repulsion is observed between $C_{60}^{\bullet -}$ and $Co^{II}TPP$. The repulsion of negative charges defines to a greater extent the stability of σ-bonded structures formed by fullerene anions. For example, the increase in the distance between the charges in the $(C_{70}^-)_2$ or $(C_{60}CN_2^-)_2$ dimers provides higher dissociation temperatures (up to 360–390 K).[27]

We obtained a new ionic complex of C_{60}^{-} with Co^{II}TPP and {cryptand[2,2,2]·(Na$^+$)} cations. The complex contains coordination {Co^{II}TPP·(C_{60}^{-})} units bonded by Co–C bonds of 2.262(2) Å (100 K). Short Co–C bonds and vdW interactions with the environment provides an opportunity for the first time to study an ordered structure of such coordination units. A temperature increase to 250 K elongates the Co–C bonds and induces disorder in the crystal structure. At the formation of the coordination bonds both Co^{II}porphyrin and $C_{60}^{\bullet-}$ spins are paired and the complex manifests diamagnetic behavior. Their dissociation restores paramagnetic Co^{II}porphyrin and $C_{60}^{\bullet-}$ species. Therefore, stability of the metal–carbon bond can be monitored by temperature dependent magnetic measurements. Magnetic susceptibility of the complex increases and a new EPR signal appears above 320 K indicating the beginning of dissociation of the {Co^{II}TPP·(C_{60}^{-})} units. This temperature is essentially higher than that which was observed for negatively charged $(C_{60}^{-})_2$ dimers bonded by one C–C bond (130–280 K).[18,20–27]

Experimental

Materials

Cryptand[2,2,2] and sodium ethanethiolate (CH_3CH_2SNa) were purchased from Aldrich. C_{60} of 99.98% purity was received from MTR Ltd. Solvents were purified in an argon atmosphere. *o*-Dichlorobenzene ($C_6H_4Cl_2$) was distilled over CaH_2 under reduced pressure and hexane was distilled over Na/benzophenone. The solvents were degassed and stored in a glove box. All manipulations for the synthesis of **1** were carried out in a MBraun 150B-G glove box with a controlled atmosphere, and the content of H_2O and O_2 was less than 1 ppm. The crystals were stored in the glove box and sealed in anaerobic conditions in 2 mm quartz tubes for SQUID and EPR measurements under 10^{-5} Torr. KBr pellets for IR- and UV-visible-NIR measurements were prepared in the glove box.

Synthesis

The crystals of **1** were obtained by diffusion. C_{60} (25 mg, 0.035 mmol), a 10-fold molar excess of CH_3CH_2SNa (30 mg, 0.36 mmol) and one molar equivalent of cryptand[2,2,2] (13.2 mg, 0.035 mmol) were stirred in $C_6H_4Cl_2$ (16 mL) for 2 h at 60 °C. The color of the solution changed from violet to violet-brown upon stirring. The NIR spectrum of the solution indicated the reduction of C_{60} to the −1 charged state. Co^{II}TPP was dissolved in the obtained solution, which was then cooled down, filtered in a 50 mL glass tube of 1.8 cm diameter with a ground glass plug, and 30 mL of hexane was layered over the solution. Diffusion was carried out during 1 month to yield the crystals of **1** on the wall of the tube. The solvent was decanted from the crystals, which were washed with hexane to give black prisms up to $1 \times 1 \times 0.5$ mm^3 in size with 70% yield. The composition of the complex was determined from the X-ray diffraction on a single crystal: {cryptand[2,2,2]·(Na$^+$)}·{Co^{II}TPP·(C_{60}^{-})}·$(C_6H_4Cl_2)_2$ (**1**). Several single crystals selected from the synthesis had the same unit cell parameters.

General

UV-visible-NIR spectra were measured in KBr pellets on a Shimadzu-3100 spectrometer in the 240–2600 nm range. FT-IR spectra were measured in KBr pellets with a Perkin-Elmer 1000 Series spectrometer (400–7800 cm^{-1}). EPR spectra were recorded for a polycrystalline sample from 4 up to 360 K with a JEOL JES-TE 200 X-band ESR spectrometer equipped with a JEOL ES-CT470 cryostat. A Quantum Design MPMS-XL SQUID magnetometer was used to measure static susceptibility of polycrystalline **1** between 400 and 1.9 K at 100 mT static magnetic field. A sample holder contribution and core temperature independent diamagnetic susceptibility (χ_0) were subtracted from the experimental data. The values of C, Θ and χ_0 were calculated in a high-temperature range with an appropriate formula: $\chi_M = C/(T - \Theta) + \chi_0$ by using experimental data in the 10–320 K range.

X-Ray crystal structure determination

Crystal data of **1** at 100(2) K: $C_{134}H_{72}Cl_4CoN_6NaO_6$, M_r = 2085.70 g mol^{-1}, black prisms, orthorhombic, $P2_12_12_1$, a = 18.4180(10), b = 19.9030(10), c = 25.1270(10) Å, V = 9210.9(8) Å^3, Z = 4, d_{calc} = 1.504 g cm^{-3}, μ = 0.379 mm^{-1}, $F(000)$ = 4288, T = 100(2) K, $2\theta_{max}$ = 54.46°, reflections measured 37 785, unique reflections 20 404, reflections with $I > 2\sigma(I)$ = 17 820, parameters refined 1407, restrains 126, R_1 = 0.046, wR_2 = 0.1215, GOF = 1.014. CCDC reference number is 721101.†

Crystal data of **1** at 250(2) K: $C_{134}H_{72}Cl_4CoN_6NaO_6$, M_r = 2085.70 g mol^{-1}, black prisms, orthorhombic, $P2_12_12_1$, a = 18.6600(10), b = 20.1340(10), c = 25.1690(10) Å, V = 9456.0(8) Å^3, Z = 4, d_{calc} = 1.465 g cm^{-3}, μ = 0.370 mm^{-1}, $F(000)$ = 4288, T = 250(2) K, $2\theta_{max}$ = 52.16°, reflections measured 34 543, unique reflections 18 499, reflections with $I > 2\sigma(I)$ = 12 864, parameters refined 2005, restrains 8925, R_1 = 0.0718, wR_2 = 0.2078, GOF = 0.870. CCDC reference number is 721102.†

The intensity data for **1** were collected on a MAC Science DIP-2020K oscillator type X-ray imaging plate diffractometer with graphite monochromated Mo Kα radiation at low temperatures using an Oxford Cryostream cooling system. Raw data reduction to F^2 was carried out using the DENZO program.[28] The structures were solved by direct method and refined by the full-matrix least-squares method against F^2 using SHELX-97.[29] Non-hydrogen atoms were refined in the anisotropic approximation. The positions of hydrogen atoms were calculated geometrically. Subsequently, the positions of H atoms were refined by the "riding" model with U_{iso} = 1.2 U_{eq} of the connected non-hydrogen atom.†

Disorder in the crystal structure of 1

100 K. All crystallographically independent units in **1** are ordered except one solvent $C_6H_4Cl_2$ molecule, which is disordered between two orientations with 0.522(8)/0.478(8) occupancies.

250 K. Fullerene molecules are disordered between two orientations linked by their rotation about the coordination Co–C bond by 140° with 0.610(2)/0.390(2) occupancies. Both solvent $C_6H_4Cl_2$ molecules are disordered between two orientations with 0.669(4)/0.331(4) and 0.561(15)/0.439(15) occupancies. Due to the high disorder of C_{60} and solvent molecules, to maintain reasonable values for the bond lengths and thermal parameters in the disordered groups, different SHELXL instructions were used: DFIX and SADI to keep the bond lengths close to mean values (separately for C(5)–C(6) and C(6)–C(6) bonds), and the hexagon shape in C_{60}; ISOR, DELU and SIMU to retain thermal parameters close to each other for neighbouring atoms in C_{60} and solvent molecules. It results in a large number of restraints, mainly coming from SIMU for disordered C_{60}.

Acknowledgements

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