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Magnetic properties and stability of negatively charged doubly bonded $C_{120}{}^{2-}$ dimers⁺

Dmitri V. Konarev,*^a Salavat S. Khasanov,^b Akihiro Otsuka,^c Hideki Yamochi,^c Gunzi Saito^d and Rimma N. Lyubovskaya^a

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A new ionic complex { $(MDABCO^+) \cdot Zn^{II}TMPP$ }₂· $(C_{120}^{2-}) \cdot (C_6H_4Cl_2)_{2.15}$ · $(C_6H_5CN)_{1.85}$ (1) (Zn^{II}TMPP: zinc(II) tetrakis(4-methoxyphenyl)porphyrin; MDABCO⁺: the cation of N-methyldiazabicyclooctane) has been obtained as single crystals. The complex contains negatively charged doubly bonded C_{120}^{2-} dimers whose magnetic properties have been studied. Magnetic moment of the complex is 2.69 $\mu_{\rm B}$ at 290 K indicating presence of about two spins per dimer. The dimers show narrow doublet-like EPR signal with $g_{\rm M} = 2.0014$ and the linewidth of 0.315 mT at 290 K. The data of SQUID measurements for 1 can be fitted according to the Heisenberg model for isolated antiferromagnetically interacting spin pairs with exchange interaction of $J/k_{\rm B} = -44.7$ K. The EPR signal from the dimers and magnetic susceptibility of 1 decrease below 40 K resulting in diamagnetic dilution of the sample and the appearance of triplet features of the signal. Two pairs of lines show peak separation of 5.2 and 2.6 mT and are centered at $g_T = 2.0008$. Averaged separation of 10.2 Å between two spins was estimated. Additional narrow doublet-like signal is manifested at 40 K and below. The signal was centered at $g_I = 1.9984$ (20 K) and was attributed to the impurity of non-dimerized $C_{60}^{\bullet-}$ since its intensity did not exceed 4% from that of the signal from the dimers. Heating of 1 above 380 K resulted in irreversible dissociation of the C_{120}^{2-} dimers to monomeric $C_{60}^{\bullet-}$ which was accompanied by transition from narrow to broad EPR signal. The degree of dimer-monomer conversion was 97.5% at 446 K.

Introduction

Interest to ionic fullerene compounds has been evoked by their magnetic, conducting and optical properties.^{1–3} Among a wide variety of dimeric and polymeric structures of negatively charged fullerenes some show promising physical properties.^{4–7} Fullerenes in these structures are linked by one or two intercage C–C bonds. Polymers bonded by single C–C bonds are formed in the salts containing di-, tri- and tetraanions of fullerenes. Those are linear polymers formed by C_{60}^{3-} in the Na₂Rb·C₆₀ and Li₃Cs·C₆₀ phases,⁴ zig-zag polymers formed by C_{70}^{2-} in the M·C₇₀·*n*NH₃ salts (M = Ca, Sr, and Ba)⁵ and

two-dimensional polymers formed by C_{60}^{4-} in Na₄·C₆₀.⁶ Two C–C bonds between fullerenes are formed *via* the [2+2] cycloaddition. For example, the C_{60}^{-} anions form linear metallic polymers in M·C₆₀ phases (M = K, Rb and Cs) in which each C_{60}^{-} forms four C–C bonds with neighbours.⁷ Formation of polymers through the [2+2] cycloaddition was also observed when neutral fullerenes were treated at high pressure and temperature.⁸

Fullerene dimerization is also accompanied by formation of one or two intercage C–C bonds. Neutral fullerenes form only doubly bonded C_{120} dimers.⁹ On the contrary, negatively charged fullerenes generally form diamagnetic singly bonded C_{120}^{2-} dimers (Fig. 1a) which dissociate even at 140–250 K and cannot be observed at room temperature.¹⁰ Recently ionic {(MDABCO⁺)·Co^{II}TMPP}₂·(C₁₂₀²⁻)·(C₆H₄Cl₂)_{2.5}·(C₆H₅CN)_{1.5} complex (2) (Co^{II}TMPP: cobalt(II) tetrakis(4-methoxyphenyl)porphyrin; MDABCO⁺: the cation of *N*-methyldiazabicyclooctane) has been synthesized.¹¹ The complex contains a new type of negatively charged dimers, in which fullerene anions are bound by two intercage C–C bonds (Fig. 1b). Analysis of magnetic properties of these dimers showed that in contrast to the diamagnetic single-bonded C_{120}^{2-} dimers, they contain unpaired spins. However, the presence of paramagnetic

^a Institute of Problems of Chemical Physics RAS, Chernogolovka, Moscow region, 142432, Russia. E-mail: konarev@icp.ac.ru; Fax: +7-49652-21852

^b Institute of Solid State Physics RAS, Chernogolovka, Moscow region, 142432, Russia

^c Research Center for Low Temperature and Materials Sciences,

Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

^d Research Institute, Meijo University, 1-501 Shiogamaguchi, Tempaku-ku, Nagoya, 468-8202, Japan

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Fig. 1 (a) Singly bonded C_{120}^{2-} dimer^{10b} and (b) doubly bonded C_{120}^{2-} dimer in 2.¹¹

Co^{II}TMPP in **2** does not allow investigating intrinsic magnetic properties of these dimers because of strong exchange interaction between C_{120}^{2-} and Co^{II}TMPP resulting in formation of a system of four strongly antiferromagnetically interacting S = 1/2 spins.¹¹

We have obtained a new {(MDABCO⁺)·Zn^{II}TMPP}₂· (C_{120}^{2-})·($C_6H_4Cl_2$)_{2.15}·(C_6H_5CN)_{1.85} complex (1), which also contains doubly bonded C_{120}^{2-} dimers. The IR- and UV-visible-NIR spectra of these dimers are discussed. Zn^{II}TMPP is diamagnetic and EPR silent allowing one to study the intrinsic magnetic properties of the dimers by EPR and SQUID techniques. The dissociation temperature for the dimers is determined and compared with those of other fullerene dimers.

Results and discussion

1. Synthesis

The crystals of 1 were obtained by diffusion technique. In contrast to previously described complex 2 which was prepared as a single phase,¹¹ complex 1 was obtained as a mixture of two phases (total yield is about 70%). The first minor phase (from 5 to 40% of the total amount of crystals) was obtained as good quality well-shaped elongated parallelepipeds. The second major phase contained hexagonal prisms. The surface of the prisms had low quality, even just prepared, and crystals degraded quickly. The parallelepipeds were separated from prisms under microscope in a glove box. The parallelepipeds were tested by X-ray diffraction which showed them to be isostructural to 2 and have the $\{(MDABCO^+), Zn^{II}TMPP\}_2$. $(C_{120}^{2-}) \cdot (C_6H_4Cl_2)_{2,15} (C_6H_5CN)_{1.85}$ composition (1). Prisms did not reflect in the X-ray diffraction experiment. The loss of crystallinity probably due to elimination of solvent molecules. According to SQUID and EPR measurements they are diamagnetic and EPR silent in the 2-300 K range and perhaps contain diamagnetic singly bonded $(C_{60})_2$ dimers. In contrast to prisms parallelepipeds manifest intense narrow EPR signal from room temperature (290 K) and down to 4 K. Therefore, parallelepipeds and prisms can be distinguished not only by shape, but by the difference in X-ray diffraction and EPR as well.

2. Crystal structure

Crystal structure of 1 was studied at 120(2) K. The monoclinic unit cell of the structure contains two double C-C bonded C_{120}^{2-} dimers lying on a inversion center (Fig. 1b and 2, ellipsoids are shown with 20% probability) and four cations coordinated to metalloporphyrin by free nitrogen atom: (MDABCO⁺) ZnTMPP (Fig. 2). Solvent molecules occupy two positions. One position is occupied by the $C_6H_4Cl_2$ molecules, and the other position is shared by both C₆H₄Cl₂ and C₆H₅CN molecules at 0.075(6)/0.925(6) ratio. Such a composition assumes non-integer content of solvent in 1: $2.15(C_6H_4Cl_2)$: $1.85(C_6H_5CN)$. A 2:1 ratio between the MDABCO⁺ cations and the C_{120}^{2-} dimers corresponds to -2formal charge on the dimer. This conclusion is justified by IR- and visible-NIR spectra. The dimer has approximate (non-crystallographic) D_{2h} symmetry, the length of the intercage C-C bonds is 1.607(6) Å and the center-to-center distance between fullerenes in the dimer is 9.046 Å. Similar length of the intercage C-C bond and center-to-center distance were found for the doubly bonded $(C_{60}^{-})_2$ dimer in 2.¹¹ The observed length of the intercage C-C bond is only slightly longer than that in neutral doubly bonded C₁₂₀ dimer and the singly bonded C_{120}^{2-} dimer (1.575(7)⁹ and 1.597(7) Å,^{10b} respectively). The center-to-center distance is noticeably shorter than that in the singly bonded C_{120}^{2-} dimer (9.28 Å).^{10b}

Each C_{120}^{2-} dimer is surrounded by six (MDABCO⁺). ZnTMPP units (four such units are shown in Fig. 2). Two units are facing the dimer by slightly concave porphyrin surface and four units by the MDABCO⁺ cations. The shortest Zn···C(C_{120}^{2-}) distance of 3.02–3.17 Å indicates absence of coordination between metalloporphyrin and fullerene dimer. However, multiple van der Waals N, C···C(C_{120}^{2-}) contacts between the plane of the porphyrin macrocycle and C_{120}^{2-} provide $\pi-\pi$ interaction between them. A relatively long Zn···C(C_{120}^{2-}) distance is a result of the coordination of MDABCO⁺ to ZnTMPP. The N(MDABCO⁺)···Zn distance is rather short (2.280(4) Å) and the displacement of the Zn atom from the plane of four nitrogen atoms towards MDABCO⁺ is



Fig. 2 Fragment of crystal structure of **1** showing the cage from the (MDABCO⁺)-ZnTMPP units accommodating the doubly bonded C_{120}^{2-} dimer. Only major occupied orientation of MDABCO⁺ is shown.

0.265 Å, whereas such displacement from the 24-atom porphyrin plane is 0.430 Å.

3. IR- and UV-visible-NIR spectra of 1

Detailed IR-spectrum of 1 is listed in the ESI.[†] Neutral doubly bonded C_{120} dimer has lower symmetry than pristine C_{60} and, in addition to the regular C_{60} bands at 527, 575, 1186 and 1426 cm⁻¹, shows new bands at 420, 479, 549, 612, 709, 726, 769, 796, 1462 cm^{-1.9} Formation of negatively charged C₁₂₀^{-1.9} dimers in **1** shifts the band of C_{120} at 1426 to 1387 cm⁻¹. The band of the neutral C_{120} dimer at 575 cm⁻¹ is at the same position in spectrum of 1 but is split into three components and has significantly higher intensity than the band at 527 cm^{-1} . Such changes are similar to those observed for the formation of $C_{60}^{\bullet-12}$ indicating that fullerenes in the dimers are negatively charged. Additional bands in the spectrum of C_{120}^{2-} at 420, 482, 546, 714, 794, 1462 cm⁻¹ can be attributed to symmetry forbidden silent modes of C₆₀ which appear due to the breaking of C₆₀ symmetry at dimerization. They have close positions to those observed in the spectrum of the neutral C₁₂₀ dimer.9

Spectrum of 1 in the UV-visible-NIR range is shown in Fig. 3. The doubly bonded C_{120} dimers manifest broad absorption bands at 950 and 1070 nm, which are characteristic of fullerene anions.¹³ Dimeric $C_{120}^{\bullet-}$ species photogenerated in solution from neutral C_{120} show absorption band at 1020 nm.¹⁴ The absorption bands in the visible range were attributed to Zn^{II}TMPP. Those are intense Soret band at 440 nm and Q-bands at 566 and 609 nm (Fig. 3).

4. Magnetic properties

EPR spectra of 1 were measured for one single crystal tested by X-ray diffraction and for one polycrystalline sample. Both spectra are similar and contain the same set of lines down to 4 K. Therefore the EPR responses of bulk sample and single crystal are identical. The admixture of second phase (prisms) if present in the polycrystalline sample will not contribute to the EPR signal since this phase is diamagnetic and EPR silent. Narrow intense doublet-like signal with $g_M = 2.0014$ and line width (ΔH) of 0.315 mT is observed for both samples at room temperature, RT = 290 K (Fig. 4a). The C₆₀^{•-} radical anions exhibit at RT broad EPR signals ($\Delta H = 3-6$ mT), which



Fig. 3 UV-visible-NIR spectrum of **1** in KBr pellet in the 275–1600 nm range.



Fig. 4 EPR signal from a polycrystalline sample of **1** at: (a) 290 K; (b) 40 K (below the fitting of signal by two lines is shown, for their attribution see text); (c) 20 K (the scheme for the determination of the constant of dipole splitting *D* for triplet signal.

become narrower with decreasing temperature,^{3,13} whereas the radical anions of fullerene derivatives exhibit narrow EPR signals even at RT.¹⁵ The doubly bonded C_{120}^{2-} dimer previously observed in **2** is also a fullerene derivative (the product of addition of one fullerene to another). Nevertheless, it showed a broad EPR signal in **2** at RT ($\Delta H = 3.46$ mT).¹¹ It is possible that the broadness of this signal is a result of strong antiferromagnetic exchange interaction realized between

 C_{120}^{2-} and Co^{II}TMPP. Absence of such interaction in 1 due to diamagnetism of Zn^{II}TMPP allows narrow EPR signal from C_{120}^{2-} to be observed.

Intense major line from the dimers is observed down to low temperatures (this line is labeled as $g_{\rm M}$ in the spectra of polycrystalline 1 at 290, 40, 20 K (Fig. 4) and a single crystal of 1 at 20 and 4 K (Fig. 5)). The *g*-factor and linewidth of this line are nearly temperature independent down to 4 K. However, its intensity reaches maximum at 40 K and rapidly decreases below this temperature.

Magnetic susceptibility of polycrystalline **1** was measured in the 300–1.9 K range. Magnetic moment of the complex is 2.69 $\mu_{\rm B}$ at 290 K. This value is close to the magnetic moment calculated for a system with a triplet S = 1 state (2.83 $\mu_{\rm B}$) or two noninteracting S = 1/2 spins (2.45 $\mu_{\rm B}$). The maximum of magnetic susceptibility is found near 55 K and magnetic susceptibility drops below 40 K (Fig. 6a). Observed temperature dependence of magnetic susceptibility can be fitted well by the Heisenberg model for isolated pairs of antiferromagnetically interacting spins¹⁶ with $J/k_{\rm B} = -44.7$ K (Fig. 6b).

Thus, dimer has about two spins at room temperature. Dimers have diamagnetic singlet (S = 0) ground state and antiferromagnetic ordering of spins is realized below 40 K as is shown by both EPR and SQUID measurements. Small amount of spins is still observed even at 4 K (Fig. 5b). It is interesting that triplet features of the signal from the dimers are not observed in undiluted sample from room temperature down to 40 K. Below 40 K dimers transfer to diamagnetic state and paramagnetic dimers become magnetically isolated by

a



Fig. 5 EPR spectrum of arbitrary oriented single crystal of 1 at (a) 20 K; (b) 4 K. For attribution of the signals with g_M , g_I , g_T see the text.

diamagnetic ones. Diamagnetic dilution results in manifestation of triplet features of the signals both in the EPR spectra of polycrystalline sample and single crystal. At 20 K when intensity of the major signal from the dimers decreases by a factor of 4, the triplet features are well resolved (they are even more pronounced for the spectrum of arbitrary oriented single crystal of 1, Fig. 5). Therefore, triplet features for the C_{120}^{2-} dimers can be observed in solid state only for diamagnetically diluted samples. The use of diamagnetically diluted samples to minimize the effects of intermolecular contribution among the paramagnetic centers is a common practice in the study of biradicals. Concentrated samples (crystals) can frequently show doublet-like lines, for example dianion of anthracene with triplet state or exchange coupled copper(II) nitroxide clusters.¹⁷ In the latter case diamagnetic dilution due to the spin phase transition also provides the appearance of triplet features of the EPR signal.^{17b} Parameters of the triplet signal were estimated from the spectrum of polycrystalline sample of 1 at 20 K. The signal consists of two pairs of lines with approximate peak separation of 5.2 and 2.6 mT. Constant D of the dipole interaction was estimated from the peak separation to be D = 2.6 mT (Fig. 4c). Averaged separation between two spins in the point-dipole approximation was calculated to be 10.2 Å which is a reasonable value for the fullerene dimer. The g-factor of the signal is slightly shifted relative to the high-temperature major signal with g_M and is equal to $g_{\rm T} = 2.0008$.

The most actively studied negatively charged fullerene dimer is $C_{120}O^{2-}$ which has spin state S = 1.¹⁸ The spectrum of this dimer was measured in dilute solution. It is very similar to that of the doubly bonded C_{120}^{2-} dimer at 20 K. It manifests a central doublet-like line with g = 2.0018 which is surrounded by triplet features centered at g = 2.0007 and having the dipole interaction constant D = 2.6 mT.¹⁸ Thus, the distances between the spins in the C_{120}^{2-} are comparable to that in the $C_{120}O^{2-}$ dimers.

In addition to signals attributed to the dimers, a weak doublet-like signal appears at $T \leq 40$ K. This minor signal is labelled as $g_{\rm I}$ in Fig. 4b and 5b. It is narrow ($\Delta H = 0.24$ mT at 40, 20 and 4 K) and has $g_{\rm I} = 1.9984$. The comparison of integral intensities of the minor and major signals at 40 K (when the major signal from the dimers has maximum intensity) showed that the intensity of the minor signal is only about 4% of the major signal. However, at 20 K the minor signal can be well resolved as it grows by a factor of 2 in intensity in accordance with paramagnetic temperature dependence, whereas the major signal decreases in intensity by a factor of 4 (Fig. 4c and 5a).

Contribution from the dimers strongly decreases at low temperatures (T < 20 K) and the paramagnetic tail is well pronounced in SQUID measurements (Fig. 6b, black circles). It can be fitted well by the Curie–Weiss expression with the Curie constant C = 0.039 emu K mol⁻¹ and the Weiss temperature of -1.5 K. The amount of Curie impurities was estimated to be about 4% of the total amount of fullerenes. Small Weiss temperature indicates weak magnetic interaction between these spins in contrast to strong antiferromagnetic exchange interaction observed for the spins localized on the C_{120}^{2-} dimers. The paramagnetic tail can be associated with



Fig. 6 (a) Temperature dependence of molar magnetic susceptibility of **1** in the 1.9–100 K range. Inset shows the temperature dependence of $\chi_M T$ (b) Theoretical fitting of the experimental curve by two contributions: the major contribution from the dimers (crosses) fitted by the Heisenberg model for the pairs of antiferromagnetically interacting spins with $J/k_B = -44.7$ K (squares) and the paramagnetic tail (black circles) fitted by the Curie–Weiss expression with C = 0.039 emu K mol⁻¹ and $\Theta = -1.5$ K.

minor EPR signal manifested at $T \le 40$ K which also has paramagnetic temperature dependence down to 4 K.

Spins contributed to the minor EPR signal and paramagnetic tail most probably originated from low concentration impurities. Due to specific *g*-factor value, these impurities were attributed to non-dimerized $C_{60}^{\bullet-}$ radical anions which show EPR signals with *g*-factors in the 2.000–1.996 range. Signals from $C_{60}^{\bullet-}$ can also be narrow below 20 K.^{3,13} Generally anions of fullerene derivatives including dianions of fullerene dimers show signals with *g*-factor higher than 2.000.^{15,18} It was shown¹⁰ that weak EPR signals from monomeric $C_{60}^{\bullet-}$ (from 0.5 to 5% of a total amount of fullerenes) remain after dimerization of $C_{60}^{\bullet-}$ in ionic complexes.

Crystal of 1 indicates high thermal stability of the doubly bonded C_{120}^{2-} dimers upon heating. Intensity of the narrow EPR signal decreases above 380 K and a new broad signal appears (Fig. 7). According to g-factor and linewidth, new signal can be attributed to monomeric $C_{60}^{\bullet-}$ (g = 2.0000 and $\Delta H = 3.8$ mT at 446 K, Fig. 7) which forms after dissociation of the C_{120}^{2-} dimers. The degree of conversion of the dimers to monomers was estimated to be 97.5% at 446 K



Fig. 7 (a) The EPR signal from a single crystal of **1** at 446 K. (b) The fitting of the signal by two Lorentzian lines is shown below, the attribution of the signals is in the text).

(determined from relative integral intensities of the signals). Dissociation of the dimers is irreversible because the narrow signal does not reappear when the crystal is cooled down to RT and only the signal from $C_{60}^{\bullet-}$ can be seen. Probably the dissociation temperature of the dimers in 1 is too high and the solvent molecules are removed from the crystal resulting in loss of crystallinity of the sample. Indeed, according to X-ray diffraction measurements the single crystal slowly loses crystallinity at 400 K.

Thus, the doubly bonded C_{120}^{2-} dimers are essentially more thermodynamically stable than the singly bonded ones which start dissociating at 140–250 K.¹⁰ Stability of the doubly bonded C_{120}^{2-} dimers is close to those of the singly bonded C_{140}^{2-} and $(C_{60}CN_2^{-})_2$ dimers which dissociate above 360 K¹⁹ and 380 K,²⁰ respectively. Dissociation temperature of the neutral doubly bonded C_{120} dimers is even higher (423–448 K)⁹ indicating destabilization of the negatively charged dimers relative to the neutral ones due to the repulsion of electrons.

In spite of lower stability mainly singly bonded C_{120}^{2-} dimers are formed in ionic complexes,¹⁰ whereas the doubly bonded C_{120}^{2-} dimers were found only in two ionic complexes with porphyrins. In one case both single and doubly bonded C_{120}^{2-} dimers were found in the ionic complex with manganese(II) tetraphenylporphyrin.²¹ One possible reason for formation of the doubly bonded $C_{120}{}^{2-}$ dimers in these complexes is formation of porphyrin cages which accommodate fullerene dimers. These cages are held together by van der Waals forces and can perform as a pressure cell for the dimers. This assists in formation of more compact doubly bonded dimers instead of singly bonded ones. Stability of the doubly bonded dimers is associated not only with their intrinsic stability but with presence of a porphyrin cage which can prevent dissociation of the dimer. After the crystal loses crystallinity and the porphyrin cage is decomposed when sample is heated above 400 K, the dimers cannot form again at cooling.

New complex 1 containing doubly bonded C_{120}^{2-} dimers was obtained. The dimer has D_{2h} symmetry, the intercage C–C bond of 1.607(6) Å length and center-to-center distance between fullerenes of 9.046 Å. The IR-spectrum of the dimers shows additional absorption bands due to breaking of C_{60} symmetry at dimerization and some bands are shifted relative to those of the neutral C120 dimer due to formation of fullerene anions. The bands at 950 and 1070 nm in the visible-NIR spectrum of 1 are also characteristic of fullerene monoanions. Magnetic moment of 1 is 2.69 μ_B at 290 K indicating the presence of about two spins per dimer. Magnetic behaviour of the dimers is described well by the Heisenberg model for isolated pairs of antiferromagnetically interacting spins with $J/k_{\rm B} = -44.7$ K. The dimers show a narrow doublet-like signal with $g_{\rm M} = 2.0014$ at 290 K. Intensity of this signal decreases abruptly below 40 K resulting in diamagnetic dilution of the sample and the appearance of triplet features. Dipole interaction constant D was estimated to be 2.6 and the averaged spin separation was 10.2 Å. The new minor signal with $g_I = 1.9984$ that appears below 40 K was attributed to impurity of non-dimerized $C_{60}^{\bullet-}$. The doubly bonded dimers have high thermal stability and begin to dissociate only above 380 K, whereas the singly bonded C_{120}^{2-} dimers begin to dissociate at 140-250 K. Presence of unpaired spins in a dimer in a wide range of temperature between 40 and 380 K can provide superior magnetic and conductive properties of the compounds containing such dimers.

Experimental

Materials

H₂TMPP and sodium ethanethiolate (CH₃CH₂SNa) were purchased from Aldrich. C₆₀ of 99.98% purity was received from MTR Ltd. Solvents were purified in argon atmosphere. *o*-Dichlorobenzene (C₆H₄Cl₂) was distilled over CaH₂ under reduced pressure, benzonitrile (C₆H₅CN) was distilled over Na under reduced pressure, and hexane was distilled over Na/benzophenone. The solvents were degassed and stored in a glove box. All procedures for the synthesis of **1** were carried out in a MBraun 150B-G glove box with controlled atmosphere with H₂O and O₂ content less than 1 ppm.

Synthesis

Synthesis of MDABCO·I was described previously.²² ZnTMPP was obtained in a standard procedure used for preparation of metalloporphyrins.²³ One gram of H₂TMPP was boiled with 5-fold molar excess of ZnCl₂ in *N*,*N*-dimethyl-formamide (40 ml) under argon for 30 min. The mixture was cooled down, and 100 ml of cold water was added to precipitate ZnTMPP. The precipitate was filtered off, dried in vacuum for 8 h and then was used without further purification.

The crystals of **1** were obtained by diffusion technique. C_{60} (25 mg, 0.035 mmol), 10-fold molar excess of CH₃CH₂SNa (30 mg, 0.36 mmol) and 5-fold molar excess of MDABCO·I (46 mg, 0.18 mmol) were stirred in 16 ml of $C_6H_4Cl_2 : C_6H_5CN =$ 14 : 2 mixture at 60 °C for 2 h. While stirring, the colour of the

solution changed from violet to violet-brown. The solution was cooled down to RT, filtered off, and NIR spectrum of the solution was measured to show reduction of fullerene to -1 charged state. One molar equivalent of ZnTMPP was dissolved in obtained solution, which was then filtered in a 50 mL glass tube having diameter of 1.8 cm with a ground glass plug, and 30 mL of hexane was layered over the solution. The crystals grew on the walls of the tube after 1 month of diffusion. The solvent was decanted from the crystals, which were washed with hexane (the 70% yield). Study of the crystals under microscope in a glove box showed two different phases. The first major phase contained hexagonal prisms. The second minor phase (from 5 to 40% of the total amount of crystals) was good quality well-shaped elongated parallelepipeds. The parallelepiped-shaped crystals were separated from hexagonal prisms under microscope. The crystals were tested in X-ray diffraction experiment. The composition of the parallelepipedshaped crystals was determined from X-ray diffraction on a single crystal to be { $(MDABCO^+) \cdot Zn^{II}TMPP$ }₂· (C_{120}^{2-}) · $(C_6H_4Cl_2)_{2,15}(C_6H_5CN)_{1,85}$ (1). Several single crystals of these shape had similar unit cell parameters. The structure and composition of the major phase containing hexagonal prisms could not be determined correctly due to the loss of crystallinity immediately after isolation.

General procedures

EPR spectra were recorded for X-ray tested single crystals from 4 up to 446 K and for a polycrystalline sample from 4 up to 300 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 300 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.

Crystal structure determination

Crystal data for 1 at 120(2) K: $C_{255.85}H_{119.85}Cl_{4.3}N_{13.85}O_8Zn_2$, M = 3798.82, black parallelepiped, F(000) = 3898 e, monoclinic, $P2_1/n$, Z = 4, a = 13.8523(12), b = 24.2553(11), c = 25.6268(13) Å, $\beta = 100.963(6)^\circ$, V = 8453.3(9) Å³, $D_c = 1.492$ g cm⁻³, $\mu_{Mo} = 0.430$ mm⁻¹, $2\theta_{max} = 58.28^\circ$, N(unique) = 17592 (merged from 63.243 reflections, $R_{int} = 0.0550$, $R_{sig} = 0.0624$), N_0 ($I > 2\sigma(I)$) = 12.132, parameters refined 1739, restrains 1667, R = 0.0906, w $R_2 = 0.1956$, GOF = 1.062, $|\rho_{max} = 0.584$ e Å⁻³]. CCDC reference number is 735312.

The intensity data for **1** were collected on an Oxford diffraction "Gemini-R" CCD diffractometer with graphite monochromated Mo-K α radiation at low temperatures using an Oxford Instrument Cryojet system. Raw data reduction to F^2 was carried out using CrysAlisPro, Oxford Diffraction Ltd. The structures were solved by direct method and refined by the full-matrix least-squares method against F^2 using SHELX-97.²⁴ Non-hydrogen atoms were refined in the anisotropic approximation. Positions of hydrogen atoms were refined by the "riding" model with $U_{iso} = 1.2U_{eq}$ of the

connected non-hydrogen atom or as ideal CH₃ groups with $U_{\rm iso} = 1.5U_{\rm eq}$.

To keep fullerene geometry close to ideal the bond length restrains were applied in the disordered groups along with the next-neighbour distances, using the SADI SHELXL instruction. To keep the anisotropic thermal parameters of the fullerene atoms within reasonable limits the displacement components were restrained using ISOR and DELU SHELXL instructions. That results in a great number of restrains used for the refinement of the crystal structures of 1.

Molecular disordering in 1

Porphyrin molecules and fullerene dimers are ordered. The MDABCO⁺ cations are disordered between two orientations with the 0.827(6)/0.173(6) occupancies related by cation rotation about the axis passing through two nitrogen atoms of MDABCO⁺ by 60°. Solvent molecules occupy two positions. One position is occupied by the disordered C₆H₄Cl₂ molecules and the other one is shared by both disordered C₆H₄Cl₂ and C₆H₅CN molecules.

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