Dimerization of $C_{60}^{\bullet -}$ in multi-component ionic complexes with bis(ethylenedithio)tetrathiafulvalene: $(cation^+)_2 \cdot ET \cdot (C_{60}^{\bullet -})_2$†

Dmitri V. Konarev,*[ab] Salavat S. Khasanov,[ac] Gunzi Saito,*[a] Akihiro Otsuka[d] and Rimma N. Lyubovskaya[b]

Received 22nd March 2007, Accepted 2nd July 2007
First published as an Advance Article on the web 1st August 2007
DOI: 10.1039/b704371f

Two multi-component ionic complexes $(cation^+)_2 \cdot ET \cdot (C_{60}^{\bullet -})_2$ comprising $C_{60}^{\bullet -}$ radical anions, neutral bis(ethylenedithio)tetrathiafulvalene (ET) molecules and *N*-methyldiazabicyclooctane (**1**) or *N*,*N*-dimethylpyrrolidine (**2**) cations were obtained. At room temperature **1** involves monomeric nearly freely rotating $C_{60}^{\bullet -}$ radical anions arranged in zigzag double chains passing along the *a* axis and separated by ET molecules and cations. Dimerization is observed in **1** at 280–250 K within $C_{60}^{\bullet -}$ pairs with 9.922 Å center-to-center interfullerene distances. It was shown that dimerization temperatures are dependent on the initial distance between the $C_{60}^{\bullet -}$ anions in the monomeric phase, and the shortest center-to-center interfullerene distance in **1** provides the highest dimerization temperature among ionic C_{60} complexes studied so far. The crystal structure of the dimeric phase was determined at 100 K. The $(C_{60}^-)_2$ dimers are bound by one single bond of 1.589(2) Å length with an interfullerene center-to-center distance of 9.288 Å. The room temperature unit cell parameters of **2** are similar to those of **1** and dimerization is realized in this complex at 280–250 K. Dimerization is reversible in both complexes and results in the transition of the complexes from a paramagnetic to a diamagnetic state.

Introduction

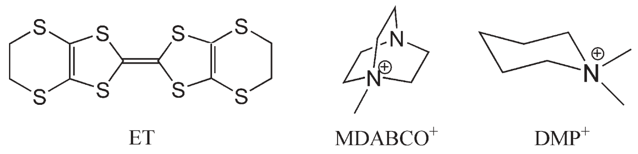
Fullerenes form a large variety of donor–acceptor complexes (D_1·fullerene) with different classes of organic and organometallic compounds such as aromatic hydrocarbons,[1,2] substituted tetrathiafulvalenes,[3,4] amines,[5] metalloporphyrins,[6–9] metal dialkyldithiocarbamates[10] and others.[11,12] Most of these complexes have a neutral ground state due to the relatively weak acceptor properties of fullerenes.[3] To obtain ionic complexes we developed a multi-component approach, in which a neutral component (D_2) co-crystallizes with a radical anion salt $(D_1^+) \cdot (C_{60}^-)$, or neutral C_{60} co-crystallizes with a radical cation salt $(D_1^+) \cdot (A^-)$ to form anionic and cationic multi-component compounds: $(D_1^+) \cdot (D_2) \cdot (C_{60}^-)$ or $(D_1^+) \cdot (A^-) \cdot (C_{60})$, respectively. The first attempts to synthesize such compounds consisted of gas-phase doping crystals of neutral fullerene complexes with substituted tetrathiafulvalenes or aromatic hydrocarbons with alkali metals[13–15] or iodine.[16] However, the doping does not allow the preparation of single crystals because of an inhomogeneous distribution of dopant since the temperatures used for complex doping are relatively low. Single crystals of multi-component complexes were prepared by a slow precipitation of all three components from solution. The cationic multi-component C_{60} complex comprising bis(ethylenedithio)tetrathiafulvalene (ET) radical cations, $[(ET^{\bullet +}) \cdot (I^-{}_3)] \cdot C_{60}$ was obtained by the co-crystallization of $ET \cdot I_{3.5}$ salt with C_{60} in a chlorobenzene–benzonitrile mixture[17] or by the diffusion of an acetonitrile solution of I_2 into a toluene–*o*-dichlorobenzene mixture containing C_{60} and ET.[18] The compound has a layered structure, in which closely packed neutral C_{60} and ionic $(ET^{\bullet +})$-$(I^-{}_3)$ layers are held together by van der Waals forces.[18] Related $[(OMTTF^{\bullet +}) \cdot (I^-{}_3)] \cdot C_{60}$ was obtained with octamethylenetetrathiafulvalene radical cations.[19] Due to integer charge transfer and rather long distances between radical cations these complexes do not show high conductivity ($\sigma = 1 \times 10^{-5}$ S cm^{-1}). However, the distances between radical cations are short enough to allow antiferromagnetic interactions between them.[19] Up to now multi-component anionic complexes $(D_1^+) \cdot (D_2) \cdot (C_{60}^-)$ were mainly obtained with metalloporphyrins as D_2.[20] Bulky tetrabenzyl-*p*-phenylenediamine (TBPDA) forms a series of complexes with C_{60} with the general formula: $(D_1^+) \cdot (TBPDA)_2 \cdot (C_{60}^{\bullet -})$, where D_1 is tetrakis(dimethylamino)ethylene, decamethylchromocene or decamethylcobaltocene.[21]

In this work we showed that neutral ET molecules are able to co-crystallize with the $(cation^+)(C_{60}^{\bullet -})$ salts to form anionic multi-component complexes $(cation^+)_2 \cdot ET \cdot (C_{60}^{\bullet -})_2$ (**1** and **2**), where the cations are *N*-methyldiazabicyclooctane (MDABCO$^+$) and *N*,*N*-dimethylpyrrolidine (DMP$^+$), respectively (Scheme 1). Complexes **1** and **2** were obtained as single crystals and were characterized by elemental analysis, IR and NIR spectra, and temperature dependent EPR and SQUID (ESI†). The crystal structure of **1** and the unit cell parameters of **2** were determined. Reversible dimerization of $C_{60}^{\bullet -}$ radical anions at high enough temperatures (280–250 K) was found in

---

[a] *Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan. E-mail: saito@kuchem.kyoto-u.ac.jp*
[b] *Institute of Problems of Chemical Physics RAS, Chernogolovka, Moscow region, 142432, Russia. E-mail: konarev@icp.ac.ru*
[c] *Institute of Solid State Physics RAS, Chernogolovka, Moscow region, 142432, Russia*
[d] *Research Center for Low Temperature and Materials Sciences, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan*

† Electronic supplementary information (ESI) available: IR spectra of ET, MDABCO·I, DMP·I, **1**; UV-visible-NIR spectra of **1** and **2**; EPR spectra of **1** and **2**; and changes in the EPR signal of **1** attributed to $C_{60}^{\bullet -}$ at dimerization. See DOI: 10.1039/b704371f



Scheme 1

1 and **2**, and the crystal structures of both monomeric and dimeric phases were presented for **1**. The design of different types of multi-component complexes (cationic and anionic ones) is discussed.

Results and discussion

Complexes **1** and **2** were prepared by the diffusion method. The (cation$^+$)($C_{60}^{\bullet-}$) salt and ET were co-crystallized together from an *o*-dichlobenzene–benzonitrile mixture by diffusion of hexane over 1 month. Among different cations only MDABCO$^+$ and DMP$^+$ form such complexes, but larger bis(benzene)chromium and tetrakis(dimethylamino)ethylene cations or smaller (Me_4P^+) cations form salts (D_1^+)(C_{60}^-) without inclusion of ET.

The C_{60} molecule has four IR-active F_{1u}(1–4) modes observed in the neutral state at 527, 577, 1182 and 1429 cm^{-1}, respectively. The absorption band of the F_{1u}(4) C_{60} mode, which is most sensitive to charge transfer to the C_{60} molecule,[22] is shifted to 1390 (**1**) and 1388 cm^{-1} (**2**), whereas the intensity of the absorption band of F_{1u}(2) mode (575 cm^{-1}) is essentially increased relatively that of F_{1u}(1) mode (522 and 525 cm^{-1} for **1** and **2**, respectively). Such changes were observed on the formation of $C_{60}^{\bullet-}$ in radical anion salts.[22,23] Characteristic absorption bands of $C_{60}^{\bullet-}$ were also observed in the NIR spectra of the complexes at 956, 1075 nm (**1**) and 946, 1075 nm (**2**). Therefore, **1** and **2** have ionic ground states with approximately -1 charge on the fullerene molecules. The 1 : 1 ratio between C_{60} and cations in **1** and **2** also supports this conclusion. The absence of additional absorption bands in the IR spectra of **1** and **2** (except those attributed to ET and cations) justifies the monomeric state of $C_{60}^{\bullet-}$ at room temperature.

The crystal structure of the high temperature phase of **1** was studied at 293(2) K. The $C_{60}^{\bullet-}$ radical anions are monomeric and rotationally disordered. Such type of disorder indicates nearly free rotation of the $C_{60}^{\bullet-}$ spheres. Fullerenes are packed in zigzag double chains passing along the *a* axis [Fig. 1(a)]. There are two crystallographically independent $C_{60}^{\bullet-}$. One $C_{60}^{\bullet-}$ has five neighbors in the chains and the other one has only three neighbors [Fig. 1(a)]. One center-to-center interfullerene distance between the two crystallographically independent $C_{60}^{\bullet-}$ is short (9.922 Å), whereas the rest of the center-to-center interfullerene distances are noticeably longer (9.972, 10.107 and 10.570 Å). Fullerene chains are separated from the neighboring ones by ET molecules and MDABCO$^+$ cations [Fig. 1(a)].

Below 280 K a reversible structural transformation takes place. The orthorhombic unit cell is retained but the unit cell volume decreases by about 297 Å^3. The crystal structure of the low temperature phase was studied at 100(2) K [Fig. 1(b)]. The $C_{60}^{\bullet-}$ radical anions form single-bonded (C_{60}^-)$_2$ dimers disordered between four orientations due to their rotation about a longer axis of the dimer passing through the intercage C–C bond (the occupancy factors are 0.33/0.30/0.22/0.15). The geometric parameters of the dimers were determined for the most occupied orientation. The length of the intercage C–C bond is 1.589(2) Å and the interfullerene center-to-center distance is 9.288 Å. Such parameters are close to those determined for other single-bonded (C_{60}^-)$_2$ dimers.[24,25] The comparison of the crystal structures of the monomeric and dimeric phases in **1** indicates that dimerization is realized within the $C_{60}^{\bullet-}$ pairs with the shortest center-to-center interfullerene distance of 9.922 Å, which decreases to 9.288 Å in the dimeric phase. Other center-to-center interfullerene distances change insignificantly at the dimerization [Fig. 1(a,b)]. Since dimerization is observed only in one type of $C_{60}^{\bullet-}$ pair with equal center-to-center distances, only one type of (C_{60}^-)$_2$ dimers are formed. This situation is different from that observed in the C_{60} complex with bis(benzene)chromium: [$Cr^I(C_6H_6)_2^{\bullet+}$]·($C_{60}^{\bullet-}$)·$C_6H_4Cl_2$, in which dimerization within the $C_{60}^{\bullet-}$ pairs with different center-to-center distances affords dimers with different geometric parameters and thermal stability.[25]

The $C_{60}^{\bullet-}$ pairs, in which dimerization is observed, are located close to the MDABCO$^+$ cations [Fig. 1(a,b)]. Dimerization reorients the MDABCO$^+$ cations, and their positively charged nitrogen atoms are directed and shift closer to the intercage C–C bond of the (C_{60}^-)$_2$ dimers [Fig. 1(b)]. Since negative charges in the (C_{60}^-)$_2$ dimer should be localized to a great extent near this bond, such reorientation of the MDABCO$^+$ cations is favorable for electrostatic interaction between negative and positive charges in the dimeric phase of **1**.

The ET molecules adopt a concave conformation to pack with nearly spherical C_{60}^- anions (Fig. 2). The dihedral angles between the central S_4C_2 fragment and the outer planar S_4C_2 fragments are 20.8 and 21.41° in the monomeric phase, and 21.42 and 21.79° in the dimeric phase. These angles are smaller than those in the neutral $(ET)_2{\cdot}C_{60}$ complex (23.3 and 33.6°) but noticeably larger than those in $(ET{\cdot}I_3){\cdot}C_{60}$, in which $ET^{\bullet+}$ radical cations are nearly planar (the corresponding dihedral angles were calculated to be 6.9°).[18] Concave ET molecules form two types of van der Waals contacts with C_{60}^- anions [the distances were calculated for the (C_{60}^-)$_2$ dimer in major occupied orientation]. The planar central S_4C_2 fragment of ET is located over the hexagonal ring of C_{60}^- with the S···C and C···C contacts in the 3.31–3.69 and 3.25–3.35 Å range and the dihedral angle between them 10.4° (π–π interaction, Fig. 2). There are also shortened S···C contacts between carbon atoms of the 6–5 bond of $C_{60}^-$and sulfur atoms of ET along the direction of the librational axis of 3.07–3.47 Å (n–π interaction, second ET molecule right in Fig. 2). Similar but noticeably longer S···C contacts of π–π and n–π type were found in $(ET)_2{\cdot}C_{60}$ (3.54–3.56 and 3.45–3.57 Å, respectively).[4] The $ET^{\bullet+}$ radical cations form van der Waals contacts with C_{60} in $(ET{\cdot}I_3){\cdot}C_{60}$ mainly by outer planar S_4C_2 fragments due to the planarity of the cations (the S···C distances lie in the 3.25–3.40 Å range).[18]

The crystal structure of **2** should be similar to that of **1** since both complexes have the same compositions and room

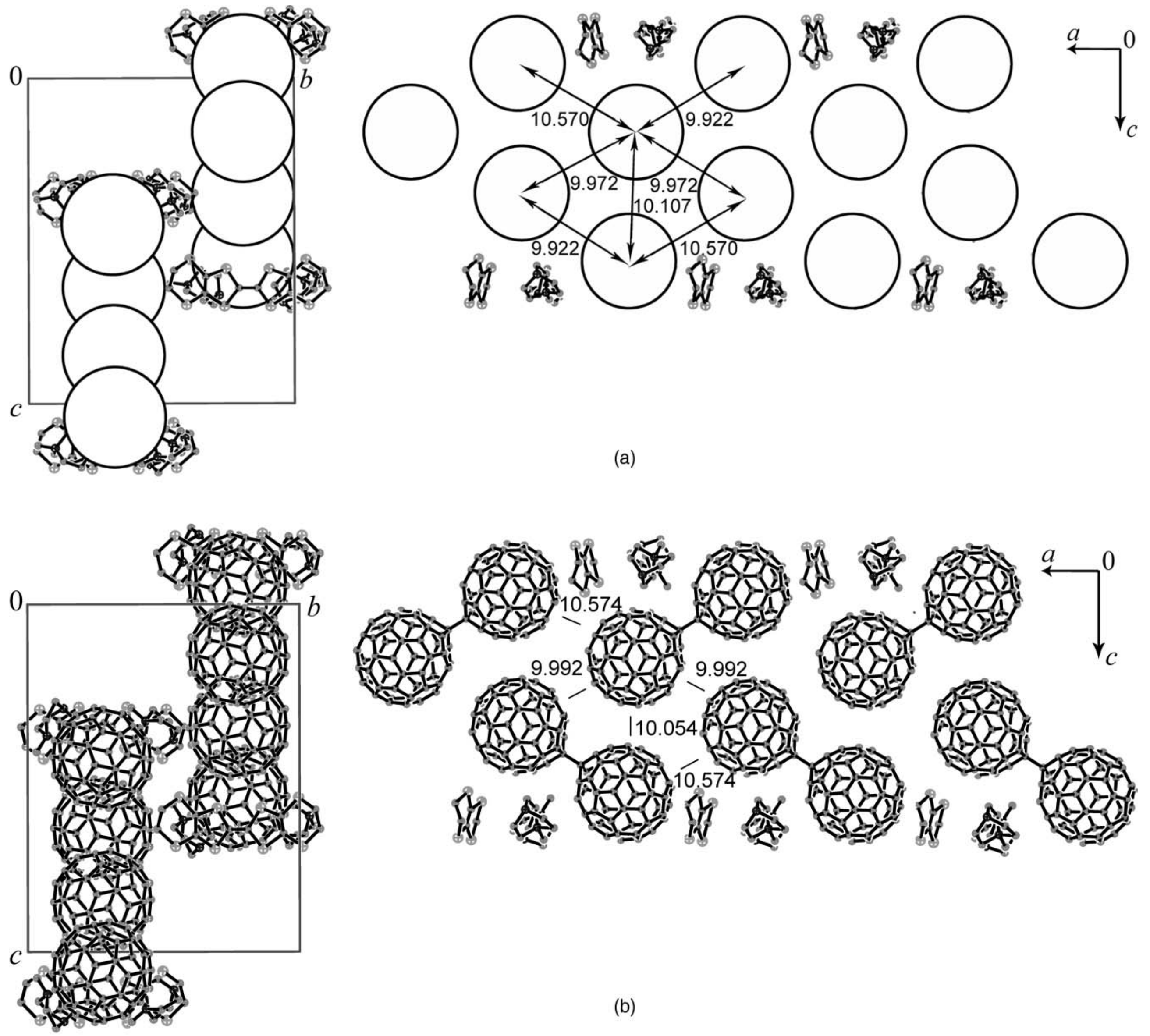


Fig. 1 Crystal structure of **1** along *a* and *b* axes: (a) monomeric phase at room temperature and (b) dimeric phase at 100(2) K. Disordered $C_{60}^{\bullet -}$ radical anions in the monomeric phase are shown by circles. Only one orientation is shown for the $(C_{60}^{-})_2$ dimers and $MDABCO^+$ cations. The numbers in the figure show the interfullerene center-to-center distances in Å.

temperature unit cell parameters of **2** (see Experimental section) are close to those of **1**.

Magnetic properties of **1** and **2** were studied by SQUID and EPR techniques. Magnetic moments of both complexes are equal to 2.37 μ_B at 340 K (**1**) and 300 K (**2**) (Fig. 3). The calculated magnetic moment for a system of two non-interacting 1/2 spins per formula unit is 2.45 μ_B. Therefore, both monomeric $C_{60}^{\bullet -}$ radical anions contribute to the magnetic moment of $(\text{cation}^+)_2\cdot ET\cdot(C_{60}^{\bullet -})_2$(**1** and **2**). Neutral ET molecules as well as $MDABCO^+$ or DMP^+ cations are diamagnetic and do not contribute to the magnetic moment. Magnetic moments of the complexes reversibly decrease approximately below 280 K due to the formation of diamagnetic $(C_{60}^{-})_2$ dimers bonded by one C–C bond. However, the dimerization temperature is so close to the room temperature value that even at 293 K several percent of the $C_{60}^{\bullet -}$ is dimerized (Fig. 3). The complexes become diamagnetic at low temperatures (T <150 K). The contribution of paramagnetic impurities below 100 K is less than 3.5% of spins from the total amount of C_{60}.

Complex **1** manifests two EPR signals. A broad signal with a *g*-factor (*g*) of 1.9999 and a linewidth (ΔH) of 3.68 mT was attributed to $C_{60}^{\bullet -}$. This signal strongly narrows with the temperature decrease, and below 280 K its integral intensity reversibly decreases more than 30 times due to dimerization. However, the signal from $C_{60}^{\bullet -}$ does not disappear completely even at low temperatures and about 3% of spins remain in the dimeric phase down to 4 K. Most probably, these spins originate from a small amount of nondimerized $C_{60}^{\bullet -}$, which remains in the sample due to the presence of defects, surface,

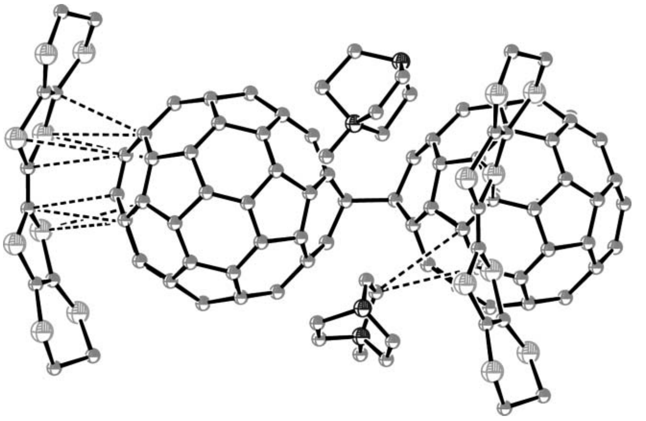


Fig. 2 Van der Waals contacts between the $(C_{60}^{-})_2$ dimers, ET molecules and $MDABCO^+$ cations.

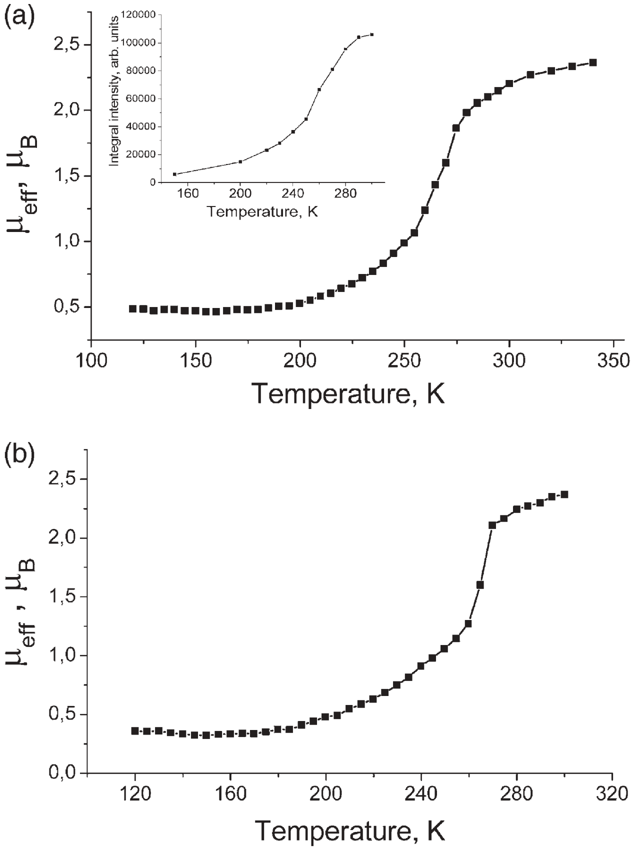


Fig. 3 Temperature dependencies of magnetic moments measured by SQUID for polycrystalline **1** (a) in the 120–340 K range (insert shows the temperature dependence of the integral intensity of $C_{60}^{\bullet -}$ EPR signal in the 150–293 K range) and **2** (b) in the 120–300 K range. The behaviour is reversible.

etc. Previously nondimerized $C_{60}^{\bullet -}$ radical anions (up to 3.3% of spins from the total amount of C_{60}) were also found in the dimeric phases of ionic C_{60} complexes.[24] A narrow signal with $g = 2.0016$ and $\Delta H = 0.2$ mT can also be resolved in the EPR spectrum of **1** (ESI†). Its integral intensity corresponds to the contribution of only 0.5% of spins from the total amount of C_{60}. This signal has a nearly temperature independent linewidth and shows a paramagnetic temperature dependence of integral intensity down to 4 K. Most probably, it appears due to the presence of $C_{120}O$ impurity, which manifests a narrow EPR signal in the reduced form.[26] We also found that a narrow EPR signal with $g = 2.0000$ and $\Delta H = 0.15$ mT strongly grew in intensity when the solution containing $C_{60}^{\bullet -}$ was exposed to air. Therefore, a narrow signal can appear due to the oxidation of a small part of $C_{60}^{\bullet -}$.[27] Complex **2** manifests an intense Lorenz line with $g = 1.9988$ and $\Delta H = 4.22$ mT ascribed to $C_{60}^{\bullet -}$. No narrow EPR signal is observed in the spectrum of **2**. The signal strongly narrows with the temperature decrease and its intensity decreases below 280 K similarly to **1**. Thus, magnetic measurements justify the dimerization of $C_{60}^{\bullet -}$ and the formation of diamagnetic EPR silent $(C_{60}^{-})_2$ dimers bonded by one C–C bond both in **1** and **2**.

In the following, we discuss the design of multi-component ionic complexes. The complexes between C_{60}^{-} anions and neutral ET molecules were for the first time prepared as crystals by direct synthesis in solution. Thus, three types of complex can be obtained for each donor–acceptor pair (for example, ET and C_{60}): a neutral two-component $(ET)_2 \cdot C_{60}$ complex, a three-component anionic complex between neutral ET and $C_{60}^{\bullet -}$ and a cationic complex between $ET^{\bullet +}$ and neutral C_{60} (their structures are shown in Fig. 4). In general, neutral complexes were prepared by co-crystallization of two components (D_2 and C_{60}). In some cases, vacancies are formed in the packing of D_2 and C_{60}, which are occupied by solvent molecules. In multi-component complexes, such vacancies should be specially formed to accommodate large third components (cations or anions). Therefore, a multi-component complex can be built for such D_2–C_{60} pairs, which are able to form a vacancy of appropriate size, mutual complimentarity between all three components of the complex being important. For example, $MDABCO^+$ and DMP^+ cations form **1** and **2** but smaller (Me_4P^+) or larger [$Cr^I(C_6H_6)_2^{\bullet +}$, $TDAE^{\bullet +}$] cations form only ET free two-component ionic $(D_1^{+}) \cdot (C_{60}^{-})$ complexes. A neutral component generally decreases the electrostatic interaction between the ionic components in $(D_1^{+}) \cdot D_2 \cdot (C_{60}^{-})$. Therefore, to promote the incorporation of this component, some additional bonding should be used between the neutral donor and one of the ionic components. In the case of **1** and **2** that is van der Waals interaction between ET and C_{60}^{-}. The driving force for the incorporation of large metalloporphyrin molecules (D_2) into the $(D_1^{+}) \cdot (C_{60}^{-})$ salts was the formation of Co–C coordination bonds between cobalt (II) porphyrins and fullerene anions[28] or the N–M coordination bonds between *N*-methyldiazabicyclooctane cations ($MDABCO^+$, Scheme 1) and metalloporphyrins.[20,29,30]

Dimerization is observed in **1** and **2** at 280–250 K. This dimerization temperature is the highest one among ionic complexes of C_{60} studied so far. The increase of dimerization temperature in **1** can be associated with small initial center-to-center distances between $C_{60}^{\bullet -}$ in the monomeric phase. Indeed, for the complexes [**1**, $Cr(C_6H_5Me)_2 \cdot C_{60}$,[31] $(Cp^*{}_2Cr) \cdot C_{60}(C_6H_4Cl_2)_2$,[25] and $Cr(C_6H_3Me_3)_2 \cdot C_{60}$[32]] with different center-to-center interfullerene distances at 293 K: $9.922 < 9.986 < 10.10 < 10.124$ Å, dimerization temperatures

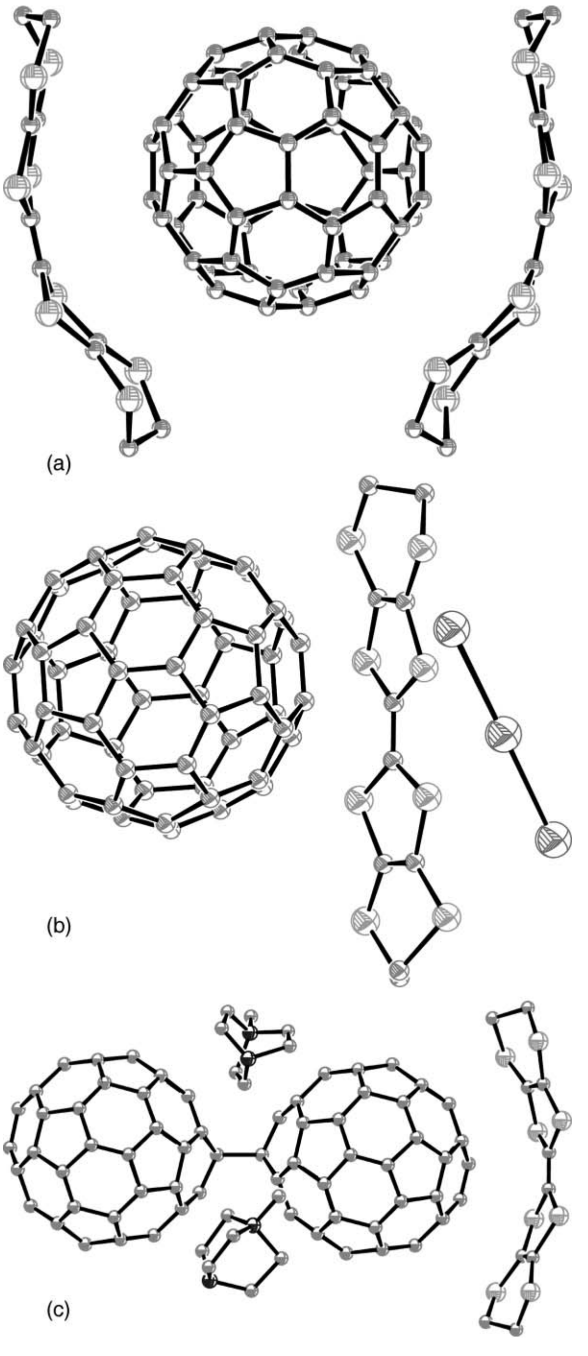


Fig. 4 Fragments of the crystal structures of three types of complex between ET and C_{60}: (a) Neutral $(ET)_2 \cdot C_{60}$, containing uncharged ET and C_{60};[4] (b) cationic $[(ET^{\bullet+}) \cdot (I^-_3)] \cdot C_{60}$, containing $ET^{\bullet+}$ cation radicals and uncharged C_{60};[18] (c) anionic $(MDABCO^+)_2 \cdot ET \cdot (C_{60}^-)_2$ (**1**), containing negatively charged $(C_{60}^-)_2$ dimers at 100(2) K and uncharged ET.

change in the reverse order: 280–250 > 250 > 220–200 > below 170 K.

Complexes under study show reversible magnetic transitions from a paramagnetic to a diamagnetic state near room temperature and can be interesting for molecular switch operating under temperature change or light excitation. The study of photodissociation of the $(C_{60}^-)_2$ dimers in **1** under light excitation is in progress.

Experimental

Materials: diazabicyclooctane (DABCO), *N*-methylpyrrolidine (MP), sodium ethanethiolate (CH_3CH_2SNa), and methyl iodide (CH_3I) were purchased from Aldrich. C_{60} of 99.98% purity was received from MTR Ltd. Solvents were purified in argon atmosphere. *o*-Dichlorobenzene ($C_6H_4Cl_2$) was distilled over CaH_2 under reduced pressure, benzonitrile (C_6H_5CN) 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 manipulations for the synthesis of **1** and **2** were carried out in an MBraun 150B-G glove box with controlled atmosphere and the content of H_2O and O_2 less than 1 ppm. The crystals were stored in a glove box and sealed in 2 mm quartz tubes for EPR and SQUID measurements under 1×10^{-5} Torr. KBr pellets for IR- and UV-visible-NIR measurements were prepared in a glove box.

General

FT-IR spectra were measured in KBr pellets with a Perkin-Elmer 1000 Series spectrometer (400–7800 cm^{-1}). UV-visible-NIR spectra were measured in KBr pellets on a Shimadzu-3100 spectrometer in the 220–1600 nm range. A Quantum Design MPMS-XL SQUID magnetometer was used to measure static susceptibilities at 100 mT magnetic field in cooling and heating conditions from 340 down to 1.9 K (**1**) and from 300 down to 1.9 K (**2**). Cooling and heating rates were 10 K min^{-1}. A sample holder contribution and core temperature independent diamagnetic susceptibility (χ_0) were subtracted from the experimental values. The χ_0 values for **1** ($\chi_0 = -8.96 \times 10^{-4}$ emu mol^{-1}) and **2** ($\chi_0 = -8.92 \times 10^{-4}$ emu mol^{-1}) were calculated using the Pascal constants. The values of -2.52×10^{-4} emu mol^{-1} for C_{60},[33] -2.02×10^{-4} emu mol^{-1} for ET,[34] and -0.95×10^{-4} emu mol^{-1} for $MDABCO^+$ and -0.93×10^{-4} emu mol^{-1} for DMP^+ were used. EPR spectra were recorded from 293 down to 4 K with a JEOL JES-TE 200 X-band ESR spectrometer.

Synthesis

N-Methyldiazabicyclooctane iodide (MDABCO·I) was obtained as described previously.[20] *N*,*N*-Dimethylpyrrolidine iodide (DMP·I) was obtained by the dropwise addition of one molar equivalent of CH_3I (1.11 mL, 0.0178 mol) to MP (1.76 g, 0.0178 mol) dissolved in 50 mL of hexane with stirring. A white crystalline precipitate of DMP·I formed during the addition. In 1 h the precipitate was filtered off, washed with 80 mL of hexane, and dried in a vacuum for 8 h. 3.9 g of DMP·I was obtained with 90% yield and satisfactory elemental analysis.

The crystals of $(MDABCO)_2 \cdot ET \cdot (C_{60})_2$ (**1**) and $(DMP)_2 \cdot ET \cdot (C_{60})_2$ (**2**) were obtained by the diffusion method. 25 mg (0.035 mmol) of C_{60}, a 10-fold molar excess of CH_3CH_2SNa (30 mg, 0.36 mmol) and a 5-fold molar excess of MDABCO·I (44.5 mg, 0.175 mmol) (**1**) or DMP·I (42.2 mg, 0.175 mmol) (**2**) were stirred in 20 mL of the $C_6H_4Cl_2$–C_6H_5CN (19 : 1) mixture for 1 h at 60 °C. During stirring the color of the solution changed from violet to red–brown. After cooling the solution down to room temperature and filtering, the NIR spectrum was measured to indicate selective reduction of C_{60} to a −1 charged state. Bis(ethylenedithio)tetrathiafulvalene (ET, 20 mg, 0.052 mmol) was dissolved in the obtained solutions at 80 °C for 2 h, then cooled down, filtered in a 50 mL glass tube of 1.8 cm diameter with a ground glass plug, and 25 mL of hexane was layered over the solution. The diffusion was carried out over 1 month to give crystals of **1** and **2** on the walls of the tube. The solvent was decanted from the crystals, which were then washed with hexane to give black elongated parallelepipeds (up to 0.3 × 0.5 × 2 mm^3 in size) with 50–60% yield.

The composition of **1** was determined according to X-ray diffraction data for a single crystal. The unit cell parameters of several selected crystals from the synthesis were the same. The composition of **2** was determined by elemental analysis. Found, %: C = 84.46, H = 2.55, N = 1.34, S = 12.05. Calc. $C_{144}H_{40}N_2S_8$, %: C = 84.25, H = 1.59, N = 1.34, S = 12.45.

X-Ray crystallography

Crystal data for **1** at 295(2) K: $C_{144}H_{38}N_4S_8$, M_r = 2080.26 g mol^{-1}, black, orthorhombic, $Pn2_1a$ (N 33), a = 17.5050(7), b = 19.4320(15), c = 24.7590(18) Å, U = 8422.0 (10) $Å^3$, Z = 4, d_{calc} = 1.641 g cm^{-3}, μ = 0.286 mm^{-1}, $F(000)$ = 4232, max. $2\theta_{max}$ = 46.92°. In total, 21 977 reflections were measured, 11 790 of which were independent. The least squares refinement on F^2 was done to $R_1[F > 2\sigma(F)]$ = 0.0706 for 7305 observed reflections, wR_2 = 0.2053 (all data), R_1 = 0.1132 for all 11 790 observed reflections with 1307 parameters and 2212 restraints; final G.O.F. = 0.962. CCDC reference number 639937.

Crystal data of **1** at 100(2) K: $C_{144}H_{38}N_4S_8$, M_r = 2080.26 g mol^{-1}, black, orthorhombic, $Pn2_1a$ (N 33), a = 17.2180(4), b = 19.3620(9), c = 24.3730(12) Å, U = 8125.3 (6) $Å^3$, Z = 4, d_{calc} = 1.701 g cm^{-3}, μ = 0.296 mm^{-1}, $F(000)$ = 4232, max. $2\theta_{max}$ = 54.54°. In total, 29 680 reflections were measured, 16 488 of which were independent. The least squares refinement on F^2 was done to $R_1[F > 2\sigma(F)]$ = 0.1142 for 11 967 observed reflections, wR_2 = 0.3478 (all data), R_1 = 0.1417 for all 16 488 observed reflections with 1857 parameters and 16 326 restraints; final G.O.F. = 1.096. CCDC reference number 639938.

The intensity data for the structural analyses were collected on a MAC Science DIP-2020 K oscillator type X-ray imaging plate diffractometer with graphite monochromated MoKα radiation at low temperatures using an Oxford Cryostream cooling system. Raw data reduction to F^2 was carried out using the DENZO program.[35] The solution and refinement of the structures were performed with SHELXTL program package.[36] The structures were refined by full-matrix least squares against F^2 of all data. Non-hydrogen atoms were refined anisotropically and isotropically for fullerene molecules at 100(2) K. Hydrogen atoms were assigned geometrically. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704371f.

Unit cell parameters for **2** were determined at 295(2) K by X-ray diffraction experiments on a single crystal. The parameters are the following: orthorhombic, a = 17.541(6), b = 19.591(6), c = 24.619(7) Å, $\alpha = \beta = \gamma = 90°$, U = 8422.0(10) $Å^3$.

Disorder in the crystal structure of **1** at 295(2) K: fullerene radical anions rotate almost freely at this temperature. Disordered fullerene molecules were approximated with 150 carbon atoms with 0.4 occupancy assigned to electron density peaks after using direct methods and consequent Fourier syntheses. Atomic coordinates and anisotropic thermal parameters for fullerene atoms were refined by a SHELXL conjugate-gradient least square procedure in the early stages and full-matrix least square procedure in final refinement, with thermal parameters fixed. One of the two $MDABCO^+$ cations is statistically disordered between two orientations.

100(2) K. The $(C_{60}{}^-)_2$ dimers are fixed in four orientations with 0.33/0.30/0.22/0.15 occupancy factors. All geometric parameters were given for the major (0.33) occupied orientation. One of two $MDABCO^+$ cations is statistically disordered between two orientations as in the monomeric phase.

Acknowledgements

The work was supported by Grant-in-Aid Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (152005019, 21st Century COE), the Russian Science Support Foundation, INTAS YSF 05-109-4653 and RFBR grants N 06-03-32824 and 06-03-91361 and Japan-Russia Research Cooperative Program.

References

1 D. V. Konarev, Y. V. Zubavichus, E. F. Valeev, Y. L. Slovokhotov, Y. M. Shul'ga and R. N. Lyubovskaya, *Synth. Met.*, 1999, **103**, 2364.
2 G. A. Domrachev, Y. A. Shevelev, V. K. Cherkasov, G. F. Fukin, G. V. Markin and A. I. Kirilov, *Russ. Chem. Bull.*, 2006, **55**, 225.
3 G. Saito, T. Teramoto, A. Otsuka, Y. Sugita, T. Ban, M. Kusunoki and K.-I. Sakaguchi, *Synth. Met.*, 1994, **64**, 359.
4 A. Izuoka, T. Tachikawa, T. Sugawara, Y. Suzuki, M. Konno, Y. Saito and H. Shinohara, *J. Chem. Soc., Chem. Commun.*, 1992, 1472.
5 D. V. Konarev, A. Y. Kovalevsky, A. L. Litvinov, N. V. Drichko, B. P. Tarasov, P. Coppens and R. N. Lyubovskaya, *J. Solid State Chem.*, 2002, **168**, 474.
6 M. M. Olmstead, D. A. Costa, K. Maitra, B. C. Noll, S. L. Phillips, P. M. Van Calcar and A. L. Balch, *J. Am. Chem. Soc.*, 1999, **121**, 7090.
7 P. D. W. Boyd, M. C. Hodgson, C. E. F. Rickard, A. G. Oliver, L. Chaker, P. J. Brothers, R. D. Bolskar, F. S. Tham and C. A. Reed, *J. Am. Chem. Soc.*, 1999, **121**, 10487.
8 D. V. Konarev, I. S. Neretin, Y. L. Slovokhotov, E. I. Yudanova, N. V. Drichko, Y. M. Shul'ga, B. P. Tarasov, L. L. Gumanov, A. S. Batsanov, J. A. K. Howard and R. N. Lyubovskaya, *Chem.–Eur. J.*, 2001, **7**, 2605.
9 T. Ishii, N. R. Kanehama, N. Aizawa, M. Yamashita, H. Matsuzaka, K. Sugiura, H. Miyasaka, T. Kodama, K. Kikuchi, I. Ikemoto, H. Tanaka, K. Marumoto and S. Kuroda, *J. Chem. Soc., Dalton Trans.*, 2001, 2975.
10 D. V. Konarev, A. Y. Kovalevsky, S. S. Khasanov, G. Saito, D. V. Lopatin, A. V. Umrikhin, A. Otsuka and R. N. Lyubovskaya, *Eur. J. Inorg. Chem.*, 2006, 1881.
11 A. L. Balch and M. M. Olmstead, *Chem. Rev.*, 1998, **98**, 2123.
12 D. V. Konarev and R. N. Lyubovskaya, *Russ. Chem. Rev.*, 1999, **68**, 19.
13 A. Otsuka, G. Saito, T. Teramoto, Y. Sugita, T. Ban, A. Zakhidov and K. Yakushi, *Mol. Cryst. Liq. Cryst.*, 1996, **264**, 345.
14 A. Otsuka, G. Saito, S. Hirate, S. Pac, T. Ishida, A. A. Zakhidov and K. Yakushi, *Mater. Res. Soc. Symp. Proc.*, 1998, **488**, 495.
15 A. Pénicaud, O. Y. Carreón, A. Perrier, D. J. Watkin and C. Coulon, *J. Mater. Chem.*, 2002, **12**, 913.

16 D. V. Konarev, E. I. Yudanova, O. S. Roschupkina, Y. M. Shul'ga, V. N. Semkin and A. Graja, *Synth. Met.*, 1997, **84**, 741.

17 D. V. Konarev, N. V. Drichko, R. N. Lyubovskaya, E. I. Yudanova, Y. M. Shul'ga, Y. V. Zubavichus and V. N. Semkin, *Russ. Chem. Bull.*, 1999, **48**, 1946.

18 D. V. Konarev, A. Y. Kovalevsky, P. Coppens and R. N. Lyubovskaya, *Chem. Commun.*, 2000, 2357.

19 D. V. Konarev, S. S. Khasanov, R. N. Lyubovskaya, A. Otsuka and G. Saito, *Synth. Met.*, 2005, **151**, 231.

20 D. V. Konarev, S. S. Khasanov, A. Otsuka, G. Saito and R. N. Lyubovskaya, *Chem.–Eur. J.*, 2006, **12**, 5225.

21 D. V. Konarev, A. Y. Kovalevsky, S. S. Khasanov, G. Saito, A. Otsuka and R. N. Lyubovskaya, *Eur. J. Inorg. Chem.*, 2005, 4822.

22 T. Picher, R. Winkler and H. Kuzmany, *Phys. Rev. B*, 1994, **49**, 15879.

23 V. N. Semkin, N. G. Spitsina, S. Krol and A. Graja, *Chem. Phys. Lett.*, 1996, **256**, 616.

24 D. V. Konarev, S. S. Khasanov, G. Saito, A. Otsuka, Y. Yoshida and R. N. Lyubovskaya, *J. Am. Chem. Soc.*, 2003, **125**, 10074.

25 D. V. Konarev, S. S. Khasanov, A. Y. Kovalevsky, G. Saito, A. Otsuka and R. N. Lyubovskaya, *Dalton Trans.*, 2006, 3716.

26 P. Paul, K.-C. Kim, D. Sun, P. D. W. Boyd and C. A. Reed, *J. Am. Chem. Soc.*, 2002, **124**, 4394.

27 A. L. Litvinov, D. V. Konarev, E. I. Yudanova, M. G. Kaplunov and R. N. Lyubovskaya, *Russ. Chem. Bull.*, 2002, **51**, 2003.

28 D. V. Konarev, S. S. Khasanov, A. Otsuka, Y. Yoshida, R. N. Lyubovskaya and G. Saito, *Chem.–Eur. J.*, 2003, **9**, 3837.

29 D. V. Konarev, S. S. Khasanov, A. Otsuka, G. Saito and R. N. Lyubovskaya, *J. Am. Chem. Soc.*, 2006, **128**, 9292.

30 D. V. Konarev, S. S. Khasanov, G. Saito, A. Otsuka and R. N. Lyubovskaya, *Inorg. Chem.*, 2007, **46**, 2261.

31 A. Hönnerscheid, L. van Wüllen, M. Jansen, J. Rahmer and M. Mehring, *J. Chem. Phys.*, 2001, **115**, 7161.

32 A. Hönnerscheid, L. van Wüllen, R. Dinnebier, M. Jansen, J. Rahmer and M. Mehring, *Phys. Chem. Chem. Phys.*, 2004, **6**, 2454.

33 R. S. Ruoff, D. Beach, J. Cuomo, T. McGuire, R. L. Whetten and F. Diederich, *J. Phys. Chem.*, 1991, **95**, 3457.

34 E. Coronado, J. Galán-Mascarós, C. Giménez-Saiz, C. J. Gómez-García and S. Triki, *J. Am. Chem. Soc.*, 1998, **120**, 4671.

35 Z. Otwinowski and W. Minor, in *Processing of X-ray diffraction data collection in oscillation mode, Methods in Enzymology*, ed. C. W. Carter and R. M. Sweet, Academic Press, New York, 1997, p. 276.

36 G. M. Sheldrick, *SHELX-97*, University of Göttingen, Germany, 1997.