

Synthesis, crystal structure and photoconductivity of the first [60]fullerene complex with metal diethyldithiocarbamate: $\{\text{Cu}^{\text{II}}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$

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The first molecular complex of fullerene C_{60} with metal dithiocarbamate, namely, $\{\text{Cu}^{\text{II}}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ (dedtc: diethyldithiocarbamate) (**1**) was obtained as single crystals. Butterfly-shaped $\text{Cu}^{\text{II}}(\text{dedtc})_2$ molecules efficiently co-crystallized with spherical fullerene molecules to form a layered structure, in which closely packed hexagonal C_{60} layers alternate with the layers composed of $\text{Cu}^{\text{II}}(\text{dedtc})_2$ dimers. The formation of the complex with C_{60} changes geometry and the EPR spectrum of starting $\text{Cu}^{\text{II}}(\text{dedtc})_2$. Magnetic susceptibility of **1** follows the Curie–Weiss law in the 300–1.9 K range with the negative Weiss constant of -2.5 K showing a weak antiferromagnetic interaction between Cu^{II} centers in the dimers. The crystals of **1** have low dark conductivity of $10^{-11} \text{ S cm}^{-1}$, which is consistent with a neutral ground state of the complex. Illumination of the crystals by white light increases the photocurrent by 20–50 times. The photoconductivity spectrum of **1** has a maximum at 470 nm showing that both intermolecular charge transfer between neighboring C_{60} molecules and photoexcitation of $\text{Cu}^{\text{II}}(\text{dedtc})_2$ can contribute to photogeneration of free charge carriers. The effect of a weak magnetic field with $B_0 < 0.5$ T on the photoconductivity of **1** has been found.

Introduction

Fullerenes have unique photoacceptor properties. Because of this fullerene containing composites with conjugated polymers, dyad and triad molecules were successfully used in the design of plastic solar cells and models of artificial photosynthesis.^{1–3} Fullerenes also form a large variety of donor–acceptor complexes with organic and organometallic donors^{4–7} such as aromatic hydrocarbons,^{8,9} substituted tetrathiafulvalenes,^{10,11} amines,^{11,12} metallocenes,^{4,5} porphyrins,^{13–17} porphyrazines,¹⁸ annulenes¹⁹ and others.^{5–7,11} Some of these complexes also show photoactive properties. Photoexcitation of neutral C_{60} complexes with amines in the solid state allows one to observe the excited ionic state by EPR spectroscopy.²⁰ The illumination of the crystals of C_{60} complexes with tetrabenzyl-*p*-phenylenediamine and tetrabenzo(1,2-bis[4*H*-thiopyran-4-ylidene]ethene) (Bz_4BTPE) by white light increases photocurrent by up to 10^3 times. In both complexes the layered structure is important for the realization of photoconductivity.^{21,22} It was also shown that free charge carriers are generated under illumination of the crystals by different ways depending on the donor used. In the case of Bz_4BTPE , which absorbs in the visible range, photoinduced electron transfer is realized by the photoexcitation of the donor molecule together with the intermolecular charge transfer (CT) between neighboring C_{60} molecules.^{21,22} A similar mechanism of photoinduced CT is realized in conjugated polymer–fullerene composites.^{1,2}

Organometallic compounds have a large potential for the design of photoactive complexes of fullerenes. However, besides porphyrins^{13–17} only a few classes of organometallic compounds have been used up to now to co-crystallize with fullerenes.^{4,5,11,18,19} One of the reasons is that a specific nearly spherical shape of fullerene molecule imposes steric demands upon the shape

of donor molecules. To effectively co-crystallize with fullerenes donor molecules must have flexible phenyl or ethyl substituents (as metal tetraphenylporphyrins or octaethylporphyrins^{13–17}) or to have concave or butterfly-like shapes of the molecules such as annulenes¹⁹, cyclotrimeratrylene^{23,24} and dianthracene.⁸ In this work we used for the first time metal(II) diethyldithiocarbamates to co-crystallize them with fullerene. Metal(II) dialkyldithiocarbamates form a wide family of organometallic donors $\text{M}^{\text{II}}(\text{R}_2\text{dte})_2$, which in most cases possess dimeric butterfly-like structure together with the presence of flexible alkyl substituents.^{25,26} These compounds vary in donor ability depending on the metal used and can easily be functionalized by changing outer substituents (R). All these facts make them promising for the design of donor–acceptor assemblies with fullerenes. It should be noted that π -complexes of metal dialkyldithiocarbamates are rare. From our knowledge only several complexes of molybdenum and tungsten dialkyldithiocarbamates with tetracyanoquinodimethane have been described.^{27,28} As we discussed above, two factors are important for photoconductivity to be realized in solid fullerene based complexes. Those are the layered structure and the presence of intense absorption of a donor component in the visible range. Because of this, among different metal(II) diethyldithiocarbamates for preparation of photoactive complex with C_{60} we chose copper(II) diethyldithiocarbamate, $\{\text{Cu}(\text{dedtc})_2\}_2$, which has an intense absorption in the visible range and dimeric structure favorable for the layered packing of fullerene molecules in a crystal.

This work reports on the first fullerene C_{60} complex with copper(II) diethyldithiocarbamate: $\{\text{Cu}^{\text{II}}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ (**1**). The synthesis, crystal structure, IR-, UV-visible, EPR spectra, and magnetic properties of **1** are presented. Photoconductivity of the crystals was studied upon illuminating them by white light. The

comparison of photoconductivity and absorption spectra of **1** allows one to suggest the mechanisms of free charge carriers generation. The effect of magnetic field with $B_0 < 0.5$ T on photoconductivity is found.

Results and discussion

The crystals of **1** were obtained by the evaporation of benzene or chlorobenzene solutions containing C_{60} and two molar equivalents of $Cu^{II}(dedtc)_2$. The crystals appeared as large black hexagonal plates. The composition of the complex was determined by elemental analysis and was justified by X-ray diffraction on a single crystal.

The complex has a monoclinic lattice. Both $Cu^{II}(dedtc)_2$ and C_{60} molecules are ordered. As a whole, **1** has a layered structure, in which hexagonal layers of closely packed C_{60} molecules alternate with those composed of $Cu^{II}(dedtc)_2$ dimers (Fig. 1a). Each C_{60} molecule has six neighbors in the layer with the shortest interfullerene center-to-center distance of 10.02 (four neighbors) and 10.25 Å (two neighbors) (Fig. 1b). In the former case the van der Waals C...C contacts between adjacent fullerenes of 3.329–3.466 Å length are shorter than the sum of van der Waals radii of two carbon atoms (3.42 Å).²⁹ The center-to-center distance of 10.02 Å is close to that in pure C_{60} crystals at 153 K (9.94 Å).³⁰

The projection of $Cu^{II}(dedtc)_2$ layer on the C_{60} layer is shown in Fig. 1b (only one $Cu^{II}(dedtc)_2$ molecule from the dimer is shown). The central CuS_4 fragments arrange exactly above C_{60} spheres, whereas flexible ethyl substituents occupy any available cavities in the C_{60} layers. The effective packing of $Cu^{II}(dedtc)_2$ and C_{60} molecules in a crystal is attained due to the slightly butterfly shape of $Cu^{II}(dedtc)_2$ molecules, which allows them to produce the cavities for C_{60} molecules

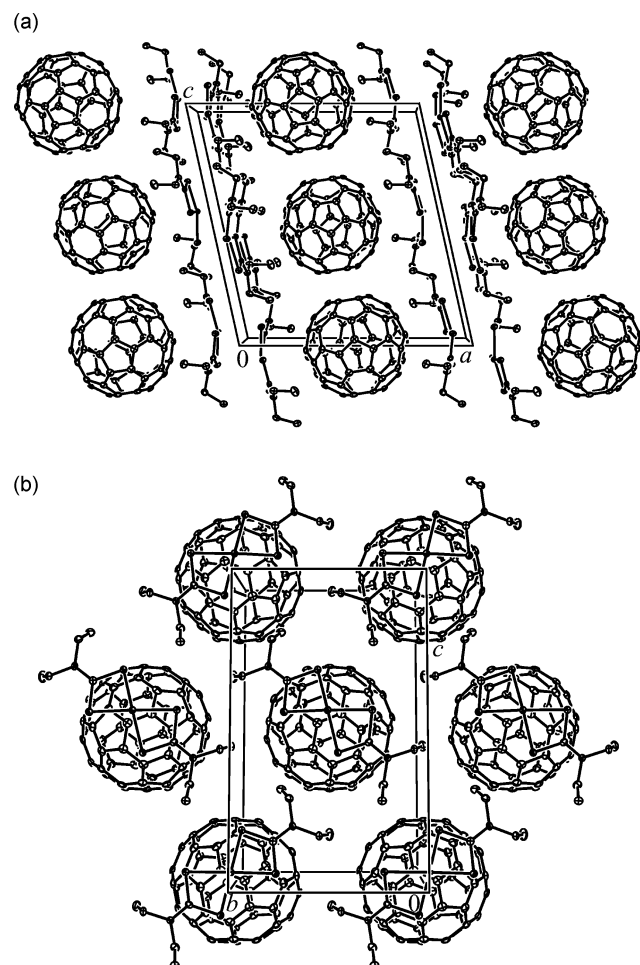


Fig. 1 The view of crystal structure of **1** along the crystallographic *b*-(a) and *a*-axes (b).

(Figs. 1a and 2a). It should be noted that planar nickel(II) diethyldithiocarbamate does not form a complex with C_{60} in similar conditions. Thus, the butterfly-like shape of $Cu^{II}(dedtc)_2$ is important for co-crystallization with fullerene. The packing $Cu^{II}(dedtc)_2$ molecules in the layer has a parquet motif (Fig. 1b). The $Cu \cdots C(C_{60})$ contacts of 3.269 and 3.307 Å length are formed with two carbon atoms of the 6–6 bond of C_{60} (Fig. 2a). These contacts are noticeably longer than those in copper(II) octaethylporphyrin or tetraphenylporphyrin complexes with fullerenes C_{60} and C_{70} (2.88–3.02 Å)^{13,15} and indicate only weak secondary metal–fullerene interaction. The van der Waals S and N...C(C_{60}) contacts lie in the 3.523–3.891 and 3.680–3.810 Å ranges (Fig. 2a). Several short H(ethyl groups of $Cu^{II}(dedtc)_2$)...C(C_{60}) of 2.845–2.938 Å length additionally stabilize this crystal structure. These contacts are mainly formed due to the C–H bonds of ethyl groups directed toward C_{60} carbons (C–H... π interaction). Thus, steric complimentary of the shapes of $Cu^{II}(dedtc)_2$ and C_{60} molecules allows the formation of multiple van der Waals contacts between them that results in the complete order of C_{60} molecules.

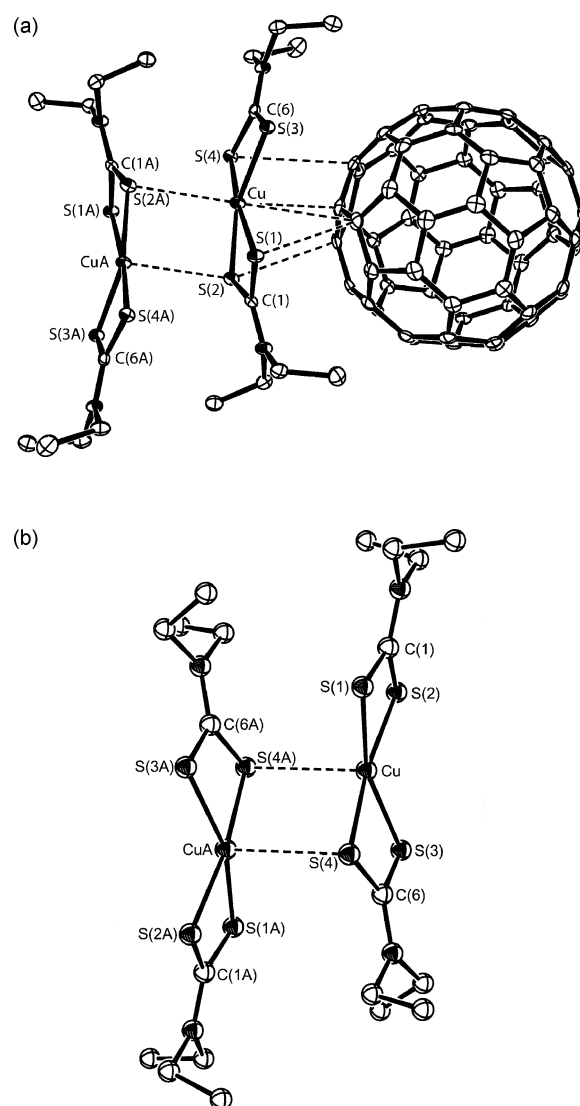


Fig. 2 The formation of van der Waals contacts between $Cu^{II}(dedtc)_2$ dimers and C_{60} molecules (dashed lines) (a) and geometry of starting $Cu^{II}(dedtc)_2$ for comparison²⁵ (b). The notation for the atoms is given for Table 1. The equivalent positions are marked by an additional letter “A” in the atom labels.

Co-crystallization of $Cu^{II}(dedtc)_2$ with a nearly spherical fullerene molecule noticeably changes its starting geometry (Table 1). The starting donor has a dimer structure with a square-pyramidal environment of Cu^{II} centers with four short equatorial

Table 1 Selected bond distances (Å) and bond angles (°) for the starting $\text{Cu}^{\text{II}}(\text{dedtc})_2$ ²⁵ and that in complex **1** (Figs 2a and 2b)

Atoms	$\text{Cu}^{\text{II}}(\text{dedtc})_2$ ²⁵	$\{\text{Cu}^{\text{II}}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ (1)
Cu–S(1)	2.3071(9)	2.3354(8)
Cu–S(2)	2.314(1)	2.2994(9)
Cu–S(3)	2.299(1)	2.2978(8)
Cu–S(4)	2.3270(9)	2.3218(8)
Cu–S(2A) CuA–S(2)		3.030(1)
Cu–S(4A) CuA–S(4)	2.844(1)	
S(1)–C(1)	1.718(3)	1.722(3)
S(3)–C(6)	1.710(3)	1.724(3)
S(1)–Cu–S(2)	77.00(3)	76.90(3)
S(3)–Cu–S(4)	76.59(3)	77.06(3)
S(1)–Cu–S(4)	102.20(3)	173.00(3)
Cu–CuA	3.572(1)	3.529(1)
Cu–S average	2.3117	2.3135

bonds (average length is 2.3117 Å) and one long axial bond of 2.844(1) Å length. Thus, the coordination number of Cu^{II} is 5.²⁵ For $\text{Cu}^{\text{II}}(\text{dedtc})_2$ in **1** the dimer structure is retained, however, the elongation of the axial coordination bond is observed up to 3.030(2) Å, whereas the equatorial bonds have nearly the same lengths (average length is 2.3135 Å). The elongation of axial Cu–S bonds can be associated with the additional weak axial coordination of Cu^{II} to the fullerene molecule, which is directed in the opposite direction to axial Cu–S bonding. The arrangement of ethyl groups of starting $\text{Cu}^{\text{II}}(\text{dedtc})_2$ is also changed at the formation of **1**. In a pure compound two ethyl groups at each nitrogen atom are directed in opposite directions (Fig. 2b) whereas, in **1** three of the four ethyl groups of $\text{Cu}^{\text{II}}(\text{dedtc})_2$ are directed in one direction towards the fullerene layer and only one ethyl group is directed in the opposite direction (Fig. 2a).

The EPR spectra of **1** and starting $\text{Cu}^{\text{II}}(\text{dedtc})_2$ at room temperature (RT = 295 K) are shown in Fig. 3. The starting donor has a broad asymmetric EPR signal with $g_1 = 2.0409$ and the line halfwidth (ΔH) of 30 G and $g_2 = 2.0613$ and $\Delta H = 48.5$ G. This signal is attributed to Cu^{II} with 1/2 ground state and is similar to the EPR signal reported previously for $\text{Cu}^{\text{II}}(\text{dedtc})_2$.²⁵ The formation of the complex noticeably changes the EPR spectrum. It becomes more asymmetric with two narrow components with $g_1 = 2.0270$ and $\Delta H = 10$ G and $g_2 = 2.0336$ and $\Delta H = 19$ G and one broad component with $g_3 = 2.0612$ and $\Delta H = 76$ G (Fig. 3b). It is seen that the component of the starting $\text{Cu}^{\text{II}}(\text{dedtc})_2$ with g_1 (2.0409) splits in **1** into two components with g_1 and g_2 (2.0270 and 2.0336), which are also shifted to the smaller g -factors, whereas the second component with g_2 (2.0613) remains nearly unchanged (2.0612). This can be attributed to changes in the local environment at Cu^{II} centers due to the elongation of the axial Cu–S bond and the appearance of weak axial coordination to the C_{60} molecule. Magnetic susceptibility of **1** follows the Curie–Weiss

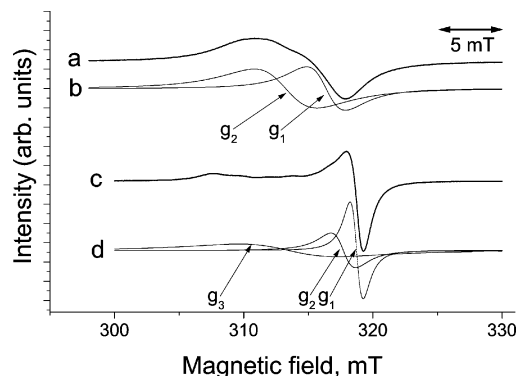


Fig. 3 EPR spectra of starting polycrystalline $\text{Cu}^{\text{II}}(\text{dedtc})_2$ (a) and polycrystalline **1** (c). The simulation of the spectra of $\text{Cu}^{\text{II}}(\text{dedtc})_2$, b) and **1**, d) by Lorentz lines is shown below.

law from 300 K down to 1.9 K with the negative Weiss constant of -2.5 K. The interaction between two Cu^{II} atoms in the $\text{Cu}^{\text{II}}(\text{dedtc})_2$ dimers can be mediated by a sulfur bridge (Cu–S–Cu path). The elongation of the axial Cu–S coordination bond hinders the magnetic interaction between two copper atoms through this bridge in spite of that formally the $\text{Cu} \cdots \text{Cu}$ distance in the $\text{Cu}^{\text{II}}(\text{dedtc})_2$ pairs in **1** is smaller (3.529 Å) than that in the starting compound (3.572 Å).²⁵

The IR spectrum of **1** (see Experimental section) indicates the neutral ground state of the complex. The UV-visible spectrum of $\text{Cu}^{\text{II}}(\text{dedtc})_2$ has a broad absorption band in the visible range with the maximum at 442 nm and a low-energy tail extended up to 600 nm (Fig. 4b). This band retains in the spectrum of **1** with the maximum at 437 nm (Fig. 4a). Two other absorption bands in the spectrum of **1** in the UV-range at 341 and 263 nm can be ascribed to intramolecular transitions in the fullerene molecule (Fig. 4a).³¹ It is also known that a relatively weak absorption band in the solid state spectrum of C_{60} at 470 nm was attributed to intermolecular CT between neighboring C_{60} molecules.³² A necessary condition for the observation of this band in the solid state spectra of the complexes is close packing of fullerene molecules in the crystal.^{11,33} Since C_{60} molecules are closely packed in the hexagonal layers of **1**, this band can also appear in the spectrum. However, it is probably overlapped with a more intense absorption band of $\text{Cu}^{\text{II}}(\text{dedtc})_2$ at 437 nm. Thus, two processes can be realized at photoexcitation of **1** in the visible range. Those are photoexcitation of $\text{Cu}^{\text{II}}(\text{dedtc})_2$ (at 437 nm) and intermolecular CT between neighboring C_{60} molecules (at 470 nm).

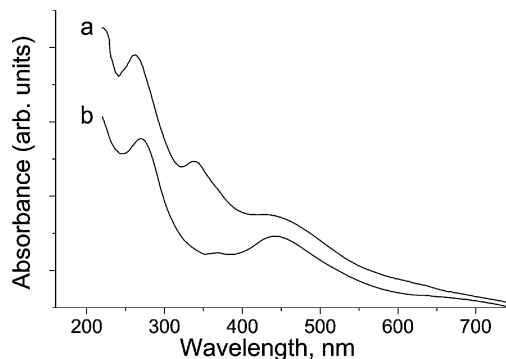


Fig. 4 Optical absorption spectra of **1** (a) and starting $\text{Cu}^{\text{II}}(\text{dedtc})_2$ (b) in KBr pellets in the 220–750 nm range.

In accordance with a neutral ground state it was found that the single crystals of **1** show low “dark” conductivity, $\sigma \sim 10^{-11} (\Omega \text{ cm})^{-1}$. Photocurrent increased by 20–50 times upon illuminating the sample with white light. These values remained unchanged under illumination for 10^4 s and were completely reproducible.

The photoconductivity spectrum of **1** is shown in Fig. 5. The signal can be simulated by two Lorentz lines with the maxima at

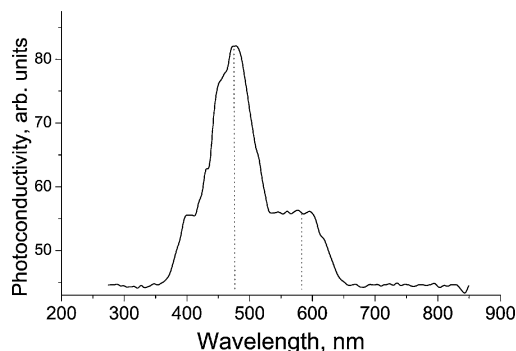


Fig. 5 The photoconductivity spectrum of **1** in the 270–850 nm range at RT.

473 and 583 nm. The main peak of photoconductivity at 473 nm has a position close to those of the absorption bands attributed previously to the photoexcitation of $\text{Cu}^{\text{II}}(\text{dedtc})_2$ (at 437 nm) and intermolecular CT between neighboring C_{60} molecules (at 470 nm). Because of this, these two processes mainly contribute to the generation of free charge carriers in **1**. It was found earlier that the second process is also contributed to photogeneration of free charge carriers in pure C_{60} crystals³⁴ and its donor–acceptor complexes^{21,22} (in all these cases photoconductivity has a peak at about 470 nm). A weaker peak of photoconductivity at 583 nm can also be associated with photoexcitation of $\text{Cu}^{\text{II}}(\text{dedtc})_2$ (which has a tail up to 600 nm) and photoexcitation of C_{60} molecules (the absorption band associated with the symmetry forbidden HOMO–LUMO transitions in C_{60} molecules has the maximum around 600 nm³¹). However, free charge carriers are not generated in the UV-range below 360 nm, where photoexcitation of C_{60} is also possible.³¹ Thus, the second weak peak can be attributed mainly to photoexcitation of $\text{Cu}^{\text{II}}(\text{dedtc})_2$.

Photoconductivity of **1** was found to be sensitive to magnetic field (MF) with $B_0 < 0.5$ T. It is seen from Fig. 6 that MF decreases the photocurrent. Such a MF dependence was previously observed in anthracene and was attributed to the effects associated with the interaction of triplet excitons with trapped charges (as a rule, those are “holes”).³⁵ This interaction releases charges from deep-seated traps and, as a result, increases the photocurrent. MF decreases the rate of the interaction of triplet excitons with trapped charges and consequently photocurrent also decreases in the MF.

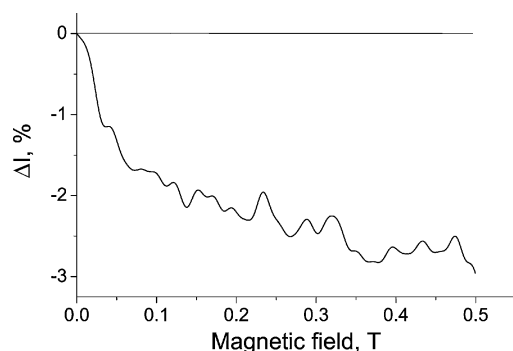


Fig. 6 The dependence of relative changes in photocurrent (ΔI) in **1** on magnetic field with the induction B_0 at RT.

Conclusion

The complex of fullerene C_{60} with copper(II) diethyldithiocarbamate: $\{\text{Cu}^{\text{II}}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ (**1**) was obtained for the first time. According to the IR- and the UV-visible-NIR spectra, **1** has a neutral ground state. X-ray diffraction on a single crystal reveals a layered structure, in which closely packed hexagonal C_{60} layers alternate with those formed by $\text{Cu}^{\text{II}}(\text{dedtc})_2$ dimers. The butterfly-like shape of the $\text{Cu}^{\text{II}}(\text{dedtc})_2$ molecules and the presence of flexible ethyl substituents is favorable for the effective packing with nearly spherical C_{60} molecules that results in the formation of multiple van der Waals contacts between them and the ordering of C_{60} molecules. Co-crystallization with C_{60} changes geometry and the EPR spectrum of $\text{Cu}^{\text{II}}(\text{dedtc})_2$. This is associated with the elongation of the axial Cu–S bond in the dimer and the appearance of additional weak coordination of Cu^{II} centers to fullerene molecules. The elongation of axial Cu–S bonds results in the decrease of magnetic interaction between Cu^{II} centers in the dimers (magnetic susceptibility of **1** follows the Curie–Weiss law down to 1.9 K with a small negative Weiss constant of -2.5 K). The crystals of **1** have low dark conductivity of 10^{-11} S cm^{-1} consistent with a neutral ground state of the complex. Illumination of the crystals by white light increases the photocurrent by 20–50 times. The photoconductivity spectrum

of **1** has a main peak at 470 nm and a weaker peak at 583 nm. The comparison of the photoconductivity spectrum with the absorption one shows that both intermolecular charge transfer between neighboring C_{60} molecules and photoexcitation of $\text{Cu}^{\text{II}}(\text{dedtc})_2$ can contribute to the photogeneration of free charge carriers in **1**. A similar mechanism of free charge carrier generation was observed previously in the C_{60} complex with Bz_4BTPE ,²² which also has absorption in the visible range, and in conjugated polymer–fullerene composites.^{1,2} An important factor for the realization of photoconductivity in **1** and in previously studied complexes $\text{TBPDA} \cdot (\text{C}_{60})_2$ and $\text{Bz}_4\text{BTPE} \cdot \text{C}_{60}$ ^{21,22} is a layered structure, in which closely packed C_{60} layers alternate with those composed of donor molecules. This is a common peculiarity of the C_{60} complexes showing photoconductivity because such an arrangement of C_{60} and donor components allows the movement of photogenerated carriers through the crystal. The effect of a weak magnetic field with $B_0 < 0.5$ T on photoconductivity of **1** was found. It is shown that the magnetic field decreases the photocurrent in contrast to $\text{Bz}_4\text{BTPE} \cdot \text{C}_{60}$, in which the magnetic field increases the photocurrent.²² In $\text{TBPDA} \cdot (\text{C}_{60})_2$ the field dependency of the photocurrent shows a sign inversion at 0.3 T, which is associated with the effect of the magnetic field on the concentration of triplet charge transfer excitons in a crystal.²¹

Experimental

Materials

$\text{Cu}^{\text{II}}(\text{dedtc})_2$ was synthesized according to ref. 25. C_{60} of 99.98% purity was used from MTR Ltd. Benzene (C_6H_6) was distilled over Na/benzophenone and chlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$) was distilled over P_2O_5 in an argon atmosphere.

Synthesis

$\{\text{Cu}^{\text{II}}(\text{dedtc})_2\}_2 \cdot \text{C}_{60}$ (**1**) was obtained by slow evaporation of benzene (30 mL) or chlorobenzene (15 mL) solution containing C_{60} (0.035 mmole, 25 mg) and 2 molar equivalents of $\text{Cu}^{\text{II}}(\text{dedtc})_2$ (0.07 mmole, 25 mg). The solvent was decanted, the crystals precipitated after one week and were washed with hexane to yield black hexagonal plates (up to $0.1 \times 0.7 \times 0.7$ mm³ size) with 70–90% yield. The IR-spectra and elemental analysis for the crystals obtained from benzene and chlorobenzene are identical indicating the formation of solvent-free complex **1** in both cases. Elemental analysis: $\text{C}_{80}\text{H}_{40}\text{N}_4\text{S}_8\text{Cu}_2$, found; %: C = 66.46, H = 3.08, N = 4.10, Cl = 0; calc., %: C = 66.70, H = 2.77, N = 3.88, S = 17.77, Cu = 8.88, Cl = 0. The composition of the complex was justified by X-ray diffraction on a single crystal. IR-spectrum of **1**: 527m, 577w, 775w, 846w, 913w, 997m, 1088w, 1147m, 1182w, 1209m, 1275s, 1356m, 1379w, 1430s, 1505s, 1603m cm^{-1} and those of starting C_{60} : 527s, 577m, 1182w, 1429s cm^{-1} and $\text{Cu}^{\text{II}}(\text{dedtc})_2$: 500w, 572w, 779w, 848m, 914m, 998m, 1078m, 1093m, 1149s, 1209s, 1273s, 1301w, 1354 m, 1378w, 1437m, 1506s, 1603w cm^{-1} .

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 on a Shimadzu-3100 spectrometer in the 220–1600 nm range. A Quantum Design MPMS-XL SQUID magnetometer was used to measure static susceptibilities down to 1.9 K. EPR spectra were recorded at room temperature with a JEOL JES-TE 200 X-band ESR spectrometer. Photoconductivity was excited using white light of a 150 W halogen tube. Photoconductivity was characterized by current I running through indium contacts attached to one of the faces of the samples with silver or carbon paste. To record the spectra a light beam of a xenon lamp was transmitted through a high-aperture monochromator. The contacts were under direct voltage of

10–50 V. A constant magnetic field with the induction up to 0.5 T was generated by an electromagnet.

X-Ray crystal structure determination

Crystal data of **1**: $\text{C}_{80}\text{H}_{40}\text{Cu}_2\text{N}_4\text{S}_8$, $M_r = 1440.72 \text{ g mol}^{-1}$, black hexagonal prisms, monoclinic, $P2_1/c$, $a = 16.1948(8)$, $b = 10.2552(5)$, $c = 17.2192(9) \text{ \AA}$, $\gamma = 102.504(2)$, $V = 2791.9(2) \text{ \AA}^3$, $Z = 2$, $d_{\text{calc}} = 1.714 \text{ g cm}^{-3}$, $\mu = 1.12 \text{ mm}^{-1}$, $F(000) = 1468$, $T = 90(1) \text{ K}$, max. $2\theta_{\text{max}} = 54.12^\circ$, reflection measured 25977, unique reflections 5683, $R_{\text{int}} = 0.036$, reflections with $I > 2\sigma(I) = 4983$, parameters refined 425, $R_1 = 0.040$, $wR_2 = 0.106$, G.O.F. = 1.082.

The X-ray diffraction data were collected at 90 K on a Bruker SMART1000 CCD diffractometer equipped with a rotating anode ($\text{Mo-K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). The data were collected by the rotation method with a 0.3° frame width (ω scan). The data collection nominally covered half of the reciprocal space by a combination of six ω scans (600 frames in each set), with different ϕ angles. Reflection intensities were integrated using the SAINT program.³⁶

The solution and refinement of the structures were performed with the SHELXTL program package.³⁷ The structures were refined by full-matrix least squares against F^2 of all data. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were partially revealed from the difference Fourier maps and refined using a “riding” model with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the connected carbon atom, and as ideal CH_3 groups with $U_{\text{iso}} = 1.5U_{\text{eq}}$ of the connected carbon atom.

CCDC reference number is 260289.

See <http://www.rsc.org/suppdata/dt/b5/b500314h/> for crystallographic data in CIF or other electronic format.

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References

- N. S. Sariciftci and A. J. Heeger, in *Handbook of Organic Conductive Molecules and Polymers*, ed. H. S. Nalwa, John Wiley and Sons Ltd., Chichester, 1997, vol. 1, p. 414.
- D. M. Guldi, *Chem. Soc. Rev.*, 2002, **31**, 22.
- D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 2001, **34**, 40.
- C. Bossard, S. Rigaut, D. Astruc, M.-H. Delvill, G. Felix, A. Fevrier-Bouvier, J. Amiel, S. Flandroids and P. Delhaes, *J. Chem. Soc., Chem. Commun.*, 1993, 333.
- A. L. Balch and M. M. Olmstead, *Chem. Rev.*, 1998, **98**, 2123.
- D. V. Konarev and R. N. Lyubovskaya, *Russ. Chem. Rev.*, 1999, **68**, 19.
- C. A. Reed and R. D. Bolskar, *Chem. Rev.*, 2000, **100**, 1075.
- D. V. Konarev, Yu. V. Zubavichus, E. F. Valeev, Yu. L. Slovokhotov, Yu. M. Shul'ga and R. N. Lyubovskaya, *Synth. Met.*, 1999, **103**, 2364.
- A. L. Litvinov, D. V. Konarev, A. Yu. Kovalevsky, I. S. Neretin, Yu. L. Slovokhotov, P. Coppens and R. N. Lyubovskaya, *CrystEngComm*, 2002, **4**, 618.
- G. Saito, T. Teramoto, A. Otsuka, Y. Sugita, T. Ban, M. Kusunoki and K. Sakaguchi, *Synth. Met.*, 1994, **64**, 359.
- D. V. Konarev, R. N. Lyubovskaya, N. V. Drichko, E. I. Yudanov, Yu. M. Shul'ga, A. L. Litvinov, V. N. Semkin and B. P. Tarasov, *J. Mater. Chem.*, 2000, 803.
- D. V. Konarev, A. Yu. Kovalevsky, A. L. Litvinov, N. V. Drichko, B. P. Tarasov, P. Coppens and R. N. Lyubovskaya, *J. Solid State Chem.*, 2002, **168**, 474.
- 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.
- 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.
- D. V. Konarev, I. S. Neretin, Yu. L. Slovokhotov, E. I. Yudanov, N. V. Drichko, Yu. 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.
- D. V. Konarev, A. Yu. Kovalevsky, X. Li, I. S. Neretin, A. L. Litvinov, N. V. Drichko, Yu. L. Slovokhotov, P. Coppens and R. N. Lyubovskaya, *Inorg. Chem.*, 2002, **41**, 3638.
- D. V. Konarev, S. S. Khasanov, G. Saito and R. N. Lyubovskaya, *J. Porphyrins Phthalocyanines*, 2003, **7**, 801.
- D. H. Hochmuth, S. L. J. Michel, A. J. P. White, D. J. Williams, A. G. M. Barrett and B. M. Hoffman, *Eur. J. Inorg. Chem.*, 2000, 593.
- P. C. Andrews, J. L. Atwood, L. J. Barbour, P. D. Croucher, P. J. Nichols, N. O. Smith, B. W. Skelton, A. H. White and C. L. Raston, *J. Chem. Soc., Dalton Trans.*, 1999, 2927.
- D. V. Konarev, G. Zerza, M. Sharber, N. S. Sariciftci and R. N. Lyubovskaya, *Synth. Met.*, 2001, **121**, 1127.
- D. V. Lopatin, V. V. Rodaev, A. V. Umrikhin, D. V. Konarev, A. L. Litvinov and R. N. Lyubovskaya, *J. Mater. Chem.*, 2005, **15**, 657.
- D. V. Konarev, S. S. Khasanov, G. Saito, D. V. Lopatin, V. V. Rodaev, A. V. Umrikhin, A. L. Litvinov and R. N. Lyubovskaya, *J. Phys. Chem. Solids*, 2005, **66**, 711.
- M. J. Hardie and C. L. Raston, *Chem Commun.*, 1999, 1153.
- D. V. Konarev, S. S. Khasanov, I. I. Vorontsov, G. Saito, Yu. A. Antipin, A. Otsuka and R. N. Lyubovskaya, *Chem. Commun.*, 2002, 2548.
- F. Jian, Z. Wang, Z. Bai, X. You, H.-K. Fun, K. Chinnakali and I. A. Razak, *Polyhedron*, 1999, **18**, 3401.
- F. Jian, Z. Wang, Z. Bai, X. You, H.-K. Fun and K. Chinnakali, *J. Chem. Cryst.*, 1999, **29**, 227.
- M. Decoster, F. Conan, J. E. Guerschais, Y. Le Mest, J. Sala Pala, J. C. Jeffery, E. Faulques, A. Leblanc and P. Molinié, *Polyhedron*, 1995, **14**, 1741.
- F. Conan, J. Sala Pala, M.-T. Garland and R. Baggio, *Inorg. Chim. Acta*, 1998, **278**, 108.
- A. Bondi, *J. Phys. Chem.*, 1966, **70**, 3006.
- H.-B. Bürgi, E. Blanc, D. Schwarzenbach, S. Liu, Y.-j. Lu, M. M. Kappers and J. A. Ibers, *Angew. Chem., Int. Ed.*, 1992, **31**, 640.
- M. S. Dresselhaus, G. Dresselhaus and P. C. Eclund, *J. Mater. Res.*, 1993, **8**, 2054.
- M. Ichida, A. Nakamura, H. Shinohara and Y. Saitoh, *Chem. Phys. Lett.*, 1998, **289**, 579.
- D. V. Konarev, N. V. Drichko, R. N. Lyubovskaya, Yu. M. Shul'ga, A. L. Litvinov, V. N. Semkin, Yu. A. Dubitsky and A. Zaopo, *J. Mol. Struct.*, 2000, **526**, 25.
- Yu. I. Golovin, D. V. Lopatin, R. K. Nikolaev, A. V. Umrikhin and S. Z. Shmurak, *Dokl. Phys.*, 2002, **47**, 849.
- V. Ern and R. E. Merrifield, *Phys. Rev. Lett.*, 1968, **21**, 609.
- SMART and SAINT, Area detector control and integration software, Version 6.01. Bruker Analytical X-ray Systems, Madison, WI, USA, 1999.
- SHELXTL, An integrated system for solving, refining and displaying crystal structures from diffraction data, Version 5.10. Bruker Analytical X-ray Systems, Madison, WI, USA, 1997.