

Synthesis, Crystal Structures, Magnetic Properties and Photoconductivity of C_{60} and C_{70} Complexes with Metal Dialkyldithiocarbamates $M(R_2dtc)_x$, where $M = Cu^{II}$, Cu^I , Ag^I , Zn^{II} , Cd^{II} , Hg^{II} , Mn^{II} , Ni^{II} , and Pt^{II} ; $R = Me$, Et , and nPr

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New complexes of fullerenes C_{60} and C_{70} with metal dialkyldithiocarbamates, $[M(R_2dtc)_x] \cdot [C_{60(70)}] \cdot [Solvent]$, $R = Et$ [$M = Cu^{II}$ (**1**; **2**), Cu^I (**3**; **4**), Ag^I (**5**), Zn^{II} (**6**), **6**), Cd^{II} (**7**; **8**), Hg^{II} (**9**), Mn^{II} (**10**), **10**), $R = Et$ and Me [$M = Cu^{II}$ (**11**), and Zn^{II} (**12**)], and $R = nPr$ [$M = Cu^{II}$ (**13**), Ni^{II} (**14**), and Pt^{II} (**15**)] were obtained. $M(R_2dtc)_x$ efficiently cocrystallized with fullerene molecules as tetrahedral monomers (**6**, **12**), dimers (**1**, **7**, **11**), and tetramers (**3**, **4**). Fullerene molecules form closely packed hexagonal and square layers in **1**, **7**, and **11**, hexagonal and tetragonal 3D structures in **6** and **12**, and island motifs in **3** and **4**. Complexes **1–15** have a neutral ground state. However, the formation of the complexes with fullerenes changes the environment of paramagnetic Cu^{II} and Mn^{II} . The EPR spectra of **1**, **2**, **11**, and **13** are essentially modified relative to those of pristine $Cu(R_2dtc)_2$ because of a weak coordination of Cu^{II} to fullerene

and a flattening of the central $(NCS_2)_2Cu$ fragments. Complex **10** shows a spectrum exhibiting features from 50 to 600 mT and manifests strong antiferromagnetic coupling of spins with a Weiss temperature of -96 K and the maximum of magnetic susceptibility at 46 K. Such magnetic behavior can be explained by the formation of $[Mn(Et_2dtc)_2]_2$ dimers in **10**. The illumination of the crystals of **1**, **2**, and **7** by white light results in up to a 10^3 increase in photocurrent. The photoconductivity spectra have maxima at 470, 450–650, and 660 nm for **1**, **2**, and **7**, respectively. Photogeneration of free charge carriers is realized by photoexcitation of $Cu(Et_2dtc)_2$ in **1** and **2**, and by charge transfer from $Cd(Et_2dtc)_2$ to C_{60} molecules in **7**. The decrease of photocurrent in **1** and **7** in a weak magnetic field with $B_0 < 0.5$ T was found.

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Introduction

Fullerenes form a wide variety of donor-acceptor complexes ranging from molecular to ionic ones^[1–3] with different classes of organic and organometallic donors: aromatic hydrocarbons,^[4] amines,^[5–7] tetrathiafulvalenes,^[6,8]

porphyrins and metalloporphyrins,^[9–11] porphyrazines,^[12] metallocenes,^[13–17] and others.^[6] Great interest in fullerene complexes was evoked by their intriguing properties. Ionic compounds show ferromagnetism^[5] and reversibly form σ -bonded structures.^[15–17] Neutral complexes were also used as templates for the preparation of fullerene polymers.^[18] They can manifest photoconductivity^[19] and excited ionic states upon photoexcitation by white light.^[20] The variation of a donor component allows one to affect the packing of fullerene molecules in a crystal, the charged state of fullerenes and, consequently, the properties of the resulting complexes. The search for new classes of donor molecules for the preparation of fullerene complexes can result in the design of new promising compounds. Recently, we have found that dimeric copper(II) diethyldithiocarbamate, $Cu(Et_2dtc)_2$, co-crystallizes with fullerenes to form a molecular complex, $[Cu(Et_2dtc)_2]_2 \cdot C_{60}$, with a layered structure.^[21] This work was extended to metal(II) dithiocarbamates with bulkier benzyl substituents (abbreviation: Bnz), namely, $Cu(Bnz_2dtc)_2$, $Ni(Bnz_2dtc)_2$, $Pd(Bnz_2dtc)_2$, and $Pt(Bnz_2dtc)_2$. They co-crystallize with C_{60} to form $M(Bnz_2dtc)_2 \cdot C_{60} \cdot (C_6H_5Cl)_{0.5}$ complexes.^[22] In contrast to dimeric $Cu(dedtc)_2$, $M(Bnz_2dtc)_2$ are monomers with planar conformation of the central $(NCS_2)_2M$ fragment, which is charac-

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teristic of Ni^{II}, Pd^{II}, and Pt^{II} dithiocarbamates.^[23–27] Moreover, Pd(Bnz₂dtc)₂ forms a multi-component ionic complex containing C₆₀ and bis(benzene)chromium ion-radicals: [Cr(C₆H₆)₂^{•+}](C₆₀^{•-})[Pd(Bnz₂dtc)₂]_{0.5}. The complex demonstrates unusual low-temperature dimerization of C₆₀^{•-} with a relatively large hysteresis and the decrease of the dimerization temperature at a fast cooling rate.^[22] Thus, metal dialkyldithiocarbamates, M(R₂dtc)_x, can successfully be used in the design of molecular and ionic complexes with fullerenes. It should be noted that although we have known about M(R₂dtc)_x for a long time, their donor-acceptor complexes with π -acceptors are rare. To our knowledge, only some complexes of molybdenum and tungsten dialkyldithiocarbamates with tetracyanoquinodimethane were described.^[28,29]

M(R₂dtc)_x can easily be modified. It is possible to vary molecular structures of M(R₂dtc)_x by changing “M” or the length of alkyl substituents (R). Donor properties of M(R₂dtc)_x can also be varied from weak donors to strong ones^[30] potentially able to ionize fullerenes. Some of M(R₂dtc)_x have broad absorption in the visible range or outstanding magnetic properties [for example, Fe^{III}-(Et₂dtc)₂Cl is the first single-component ferromagnet with $T_c = 2.46$ K]^[31] and, therefore, they can be used as light harvesting or magnetic components for the complexes.

In the present work we studied the effect of M(R₂dtc)_x (depending on M and R) on composition, structure, electronic, and physical properties of their complexes with fullerenes. We used monomeric, dimeric, and tetrameric M(R₂dtc)_x and varied the length of alkyl (R) substituents (Me, Et, and *n*Pr). M(R₂dtc)_x were both weak and strong donors. The interaction of C₆₀ with the strongest donors (Cu^I, Mn^{II}, Co^{II}, and V^{II} diethyldithiocarbamates) was studied in benzonitrile solution. Fifteen complexes of C₆₀ and C₇₀ with Cu^{II}, Cu^I, Ag^I, Zn^{II}, Cd^{II}, Hg^{II}, Mn^{II}, Ni^{II}, and Pt^{II} dialkyldithiocarbamates were obtained and characterized in the solid state. The composition of the complexes was determined from elemental analysis and X-ray diffraction on single crystals. Crystal structures of seven complexes were solved. FTIR- and UV/Visible-NIR spectra of the complexes were studied. Magnetic properties of the complexes with M(R₂dtc)_x (M = Cu^I, Cu^{II}, and Mn^{II}) were investigated by SQUID and EPR techniques. Photoconductivity of single crystals of four C₆₀ and C₇₀ complexes with Cu(Et₂dtc)₂ and Cd(Et₂dtc)₂ was studied upon illumination with white light. The comparison of the photoconductivity and the absorption spectra allows one to suggest the mechanisms of free charge carrier generation. The effect of magnetic field with $B_0 < 0.5$ T on photoconductivity was determined.

Results and Discussion

1. Interaction of Fullerenes with Metal(II) Diethyldithiocarbamates in Solution

The interaction of the strongest M(Et₂dtc)₂ donors (M = Cu^I, Mn^{II}, Co^{II}, and V^{II}) with C₆₀ was studied in solution.

C₆₀ and a fivefold molar excess of the corresponding M(Et₂dtc)_x were dissolved in benzonitrile at 60 °C over 2 h, the solutions were cooled down, filtered off, and the spectra of the resulting solutions were measured in anaerobic conditions in the 600–1600 nm range. Cu^I, Co^{II}, and V^{II} diethyldithiocarbamates reduce C₆₀ to a radical anion, and an absorption band characteristic of C₆₀^{•-} is manifested at 1070 nm. On the contrary, Mn(Et₂dtc)₂ cannot reduce C₆₀. These observations are in agreement with redox potentials of metal(II) dithiocarbamates. Related octahedral M^{III}-(dtc)₃^{1–0} (M³⁺/M²⁺ transition) are reduced at –0.77 V for V^{3+/2+}, and –0.92 V for Co^{3+/2+}, whereas the reduction potential for Mn^{3+/2+} (–0.08 V) is shifted to positive values (all vs. Ag/AgCl).^[30] C₆₀ has the first E^{0/•-} potential at –0.485 V (vs. Ag/AgCl).^[32]

2. Synthesis of Solid Complexes

The complexes obtained and the data from the elemental analysis are listed in Table 1. The ability of M(R₂dtc)_x to co-crystallize with C₆₀ and C₇₀ as well as the composition of the complexes depend on the metal (M) and the length of the alkyl substituents (R). Pristine M(R₂dtc)₂ (R = Et, *n*Pr) have different conformations of the central (NCS₂)₂M fragment. Ni(R₂dtc)₂ and Pt(R₂dtc)₂ have square planar conformation.^[23–27] Zn(R₂dtc)₂,^[33–35] Cd(R₂dtc)₂,^[36,37] and Fe(Et₂dtc)₂^[38] are dimers with a tetrahedral environment of M^{II}. Mn(Et₂dtc)₂ is a polymer with an octahedral environment of Mn^{II}.^[39] Hg(R₂dtc)₂^[40–42] and Cu(R₂dtc)₂^[43] have both square planar or square pyramidal dimeric conformations.

M(Et₂dtc)₂ (M = Cd^{II}, Hg^{II}, and Mn^{II}) co-crystallize with fullerenes in dimeric conformation to form 1:2 [C₆₀/M(R₂dtc)₂] complexes. As this takes place, Cd(Et₂dtc)₂, and Mn(Et₂dtc)₂ precipitate C₆₀ and C₇₀ complexes from C₆H₆, C₆H₅Cl, and C₆H₄Cl₂ solutions in nearly a quantitative yield [a similar ability was found for Fe(Et₂dtc)₂]. On the contrary, square planar Ni(Et₂dtc)₂, and Pt(Et₂dtc)₂ or Co(Et₂dtc)₂ and V(Et₂dtc)₂, which reduce C₆₀ in solution, do not form crystals of the complexes with fullerenes.

Elongation of alkyl substituents in M(*n*Pr₂dtc)₂ drastically changes their complex formation with fullerenes. Ni(*n*Pr₂dtc)₂ and Pt(*n*Pr₂dtc)₂ with square planar conformation form 2:1 [C₆₀/M(*n*Pr₂dtc)₂] complexes with C₆₀. Similarly, among different metal(II) dibenzylthiocarbamates only Ni(Bnz₂dtc)₂, Pd(Bnz₂dtc)₂, and Pt(Bnz₂dtc)₂ with the same conformation co-crystallize with C₆₀.^[22] It is interesting to note that Cu(R₂dtc)₂ form 1:2, 2:1, and 1:1 [C₆₀:Cu(R₂dtc)₂] complexes independently of the R (MeEt, Et, *n*Pr, and Bnz) length. It seems possible that Cu(R₂dtc)₂ in the complexes with fullerenes can adopt both square planar^[43,44] and square pyramidal dimeric conformations.^[43]

The crystals of the complexes were obtained by the evaporation of solutions containing fullerenes and corresponding donors. We used the diffusion method to prepare the complexes with air-sensitive M(R₂dtc)_x and Cd(Et₂dtc)₂.

Table 1. Data of elemental analysis for **1–15**.

		Elemental analysis found/calcd.			Cl [%]	S [%]	M [%]	Color and shape
		C [%]	H [%]	N [%]				
[Cu(Et ₂ dtc) ₂] ₂ ·C ₆₀ ^[a] [21]	1	66.46	3.08	4.10	0			black hexagonal plates
[Cu(Et ₂ dtc) ₂] ₂ ·(C ₇₀) ₂ ·(C ₆ H ₅ Cl) _{0.5}	2	66.70	2.77	3.88	0	17.77	8.88	black prisms
		83.54	2.24	1.75	0.91			
{[Cu ^I (Et ₂ dtc)] ₄ } ₅ ·(C ₆₀) ₃ ·(C ₆ H ₄ Cl ₂) ₄ ^[a]	3	83.51	1.42	1.77	1.12	8.12	4.06	black prisms
		51.71	3.11	3.75	5.58			
		50.75	3.19	4.14	4.21	18.93	18.78	
{[Cu ^I (Et ₂ dtc)] ₄ } ₅ ·(C ₇₀) ₃ ·(C ₆ H ₄ Cl ₂) ₄ ^[a]	4	53.68	2.97	3.50	4.64			black prisms
		53.26	3.03	3.93	3.93	17.97	17.83	
Ag ^I (Et ₂ dtc)·C ₆₀ ·C ₆ H ₆	5	82.14	1.48	1.33	–			black prisms
		80.85	1.52	1.32	–	6.07	10.24	
Zn(Et ₂ dtc) ₂ ·C ₆₀ ·(C ₆ H ₅ Cl) _{0.5} ·(C ₆ H ₆) _{0.5} ^[a]	6	According to X-ray diffraction data						brown prisms
{Cd(Et ₂ dtc) ₂ } ₂ ·C ₆₀ ^[a]	7	61.02	3.04	3.79	–			red-brown rhombus
		61.50	2.67	3.73	–	17.09	15.01	
{Cd(Et ₂ dtc) ₂ } ₂ ·C ₇₀	8	64.41	3.32	3.38	<0.7			red-brown rhombus
		65.20	2.41	3.33	0	15.45	13.57	
{Hg(Et ₂ dtc) ₂ } ₂ ·C ₆₀	9	56.00	2.35	3.37	–			black hexagonal plates
		55.02	2.39	3.34	–	15.29	23.96	
{Mn(Et ₂ dtc) ₂ } ₂ ·C ₇₀	10	68.88 ^[b]	2.59	3.69	0			black elongated parallelepipeds
		70.05	2.98	3.63	0	16.60	7.13	
[Cu(EtMedtc) ₂] ₂ ·C ₆₀ ^[a]	11	66.13	2.21	4.01	–			black rhombus
		65.92	2.31	4.04	–	18.49	9.24	
[Zn(EtMedtc) ₂] ₃ ·(C ₆₀) ₂ ^[a]	12	According to X-ray diffraction data						black rhombus
[Cu(<i>n</i> Pr ₂ dtc) ₂] ₂ ·(C ₆₀) ₂	13	86.74	1.48	1.44	0			thin needles
		86.67	1.51	1.51	0	6.89	3.42	
[Ni(<i>n</i> Pr ₂ dtc) ₂] ₂ ·(C ₆₀) ₂	14	87.01	1.50	1.47	0			thin needles
		86.91	1.50	1.50	0	6.88	3.21	
[Pt(<i>n</i> Pr ₂ dtc) ₂] ₂ ·(C ₆₀) ₂	15	80.81	2.30	1.70	0			thin needles
		80.93	1.41	1.41	0	6.44	9.81	

[a] The composition of the complex was proved by X-ray diffraction on single crystals. [b] A smaller content of carbon relative to the calculated values may have been caused by the addition of oxygen during elemental analysis because of the high air-sensitivity of Mn(Et₂dtc)₂.

3. Crystal Structures

Main geometric parameters of M(R₂dtc)_x and van der Waals (vdW) contacts in the complexes with fullerenes are listed in Table 2. Molecular structures of M(R₂dtc)_x are shown in Figure 1.

The crystal structure of [Cu(Et₂dtc)₂]₂·C₆₀ (**1**) has been described previously.^[21]

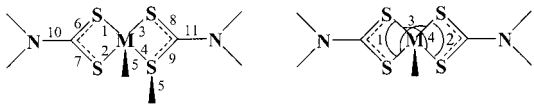
[Cd(Et₂dtc)₂]₂·C₆₀ (**7**) has a crystal structure similar to that of **1**. Cd(Et₂dtc)₂ and C₆₀ molecules are ordered at 120 K. Complex **7** has a layered structure (Figure 2, parts a and b), in which layers of closely packed C₆₀ molecules alternate with those composed of Cd(Et₂dtc)₂ dimers. Each C₆₀ molecule has four neighbors in the layer with the shortest interfullerene center-to-center distance of 9.99 Å along the diagonal to the *bc*-plane (Figure 2, b). This distance is close to that in pure C₆₀ crystals at 153 K (9.94 Å).^[45] The vdW C···C contacts are 3.33–3.77 Å. Two other neighboring fullerenes are arranged in the *c*-direction with a center-to-center distance of 10.54 Å (longer than the vdW diameter of C₆₀ molecules of 10.18 Å). Therefore, C₆₀ molecules have a square arrangement in the layers.

The projection of the Cd(Et₂dtc)₂ layer on the C₆₀ one is shown in part b of Figure 2. The central CdS₄ fragments

are arranged strictly above the C₆₀ spheres, whereas flexible ethyl substituents occupy available cavities in the C₆₀ layers. The effective packing of Cd(Et₂dtc)₂ and C₆₀ molecules in a crystal is attained due to a butterfly shape of Cd(Et₂dtc)₂ dimers (Figure 1), which allows them to encapsulate C₆₀ molecules (Figure 2, c).

The packing of Cd(Et₂dtc)₂ dimers in the layer has a parquet-like motif (Figure 2, b). The shortest Cd···C(C₆₀) contacts of 3.587 and 3.592 Å are formed with two carbon atoms of the 6–6 bond of C₆₀. These contacts are noticeably longer than the Cd···C(C₆₀) contacts in **1** (3.334 and 3.379 Å).^[21] Co-crystallization of Cd(Et₂dtc)₂ with C₆₀ does not affect its geometry. The pristine donor has a dimeric structure with a nearly tetrahedral environment of Cd^{II} with three short equatorial bonds and one short axial bond (an average length is 2.575 Å). One equatorial bond is noticeably longer than the other ones (2.812 Å).^[36] The dimeric structure of Cd(Et₂dtc)₂ is retained in **7**. Averaged lengths of three short equatorial bonds and one short axial bond are nearly the same (2.577 Å), but the long equatorial bond is elongated to 2.877 Å. Two of four ethyl groups of Cd(Et₂dtc)₂ are directed towards the fullerene layer in **7** (Figure 2, c), whereas in **1** three of four ethyl groups of Cu(Et₂dtc)₂ are directed towards the fullerene layer.^[21]

Table 2. Geometric parameters for metal dialkyldithiocarbamates in the complexes with fullerenes.



Complex Geometry	1 Dimer	11 Dimer	7 Dimer	3 Tetramer ^[a]	4 Tetramer ^[a]	6 Tetrahedral monomer	12 Tetrahedral monomer ^[b]
Bond lengths [Å]							
1	2.3354(8)	2.3057(15)	2.8771(10)	2.245(3)–	2.247(3)–	2.3449(9)	2.340(3)
2	2.2978(8)	2.3361(12)	2.544(9)	2.281(3)	2.278(3)	2.3390(9)	2.343(3)
3	2.2994(9)	2.3389(12)	2.5333(10)			2.3425(10)	2.394(3)
4	2.3218(8)	2.3177(14)	2.6330(10)			2.3350(9)	2.357(3)
5	3.030(1)	2.7869(12)	2.5988(12)			–	–
6	1.725 (3)	1.718(5)	1.758(4)			1.705(4)	1.695(13)
7	1.722(3)	1.707(5)	1.714(3)	1.700(10)–	1.698(11)–	1.735(3)	1.712(14)
8	1.720(3)	1.717(6)	1.737(3)	1.764(10)	1.777(10)	1.733(3)	1.743(12)
9	1.724(3)	1.724(5)	1.717(4)			1.733(6)	1.1.754(11)
10	1.321(4)	1.328(7)	1.337(4)	1.324(4)–	1.317(14)–	1.340(5)	1.281(14)
11	1.320(4)	1.335(7)	1.331(5)	1.335(4)	1.342(15)	1.326(4)	1.355(16)
M···S (1–4) aver.	2.3135	2.3246	2.6468	2.2567	2.2618	2.3403	2.358
Bond angles [°]							
1	76.90(3)	76.73(5)	66.67(3)	122.6(1)–	121.83(11)–	77.89(3)	78.17(12)
2	77.06(3)	76.44(5)	70.29(3)	123.18(11)	123.65(10)	78.29(3)	78.15(13)
3	164.84(3)	162.67(6)	143.80(3)			127.18(4)	129.21(13)
4	173.00(3)	169.49(5)	157.64(4)			128.19(4)	130.28(12)
M···M distances [Å]	3.529(1)	3.561(2)	3.802(2)	tetrahedron 2.5855(17)– 2.6239(17)	tetrahedron 2.5698(18)– 2.6306(18)	–	–
Donor–Fullerene interactions, shortest vdW contacts							
M···C(Ful.) [Å]	3.269, 3.307	3.334, 3.379	3.587, 3.592	4.800, 4.838	4.437, 4.476	3.659, 3.822	3.66–3.94
S···C(Ful.) [Å]	3.52–3.89	3.52–3.95	3.51–3.80	3.59–3.99	3.66–3.84	3.35–3.76	3.43–3.63
N···C(Ful.) [Å]	3.68–3.81	3.72–3.77	3.52–3.77	3.89–3.95	3.66–3.95	3.37–3.52	3.65–3.75
H···C(Ful.) [Å]	2.84–2.94	2.97–3.00	2.86–3.13	2.92–3.26	2.78–3.08	2.95–3.13	3.06–3.28
Fullerene–Fullerene interaction							
Packing of fullerenes	hexagonal layers, 6 neighbors	hexagonal layers, 6 neighbors	square layers, 4 neighbors	isolated	isolated	hexagonal, 3D, 6 neighbors	tetragonal, 3D, 4 neighbors
Interfullerene center-to-center distances [Å]	10.02 (×4), 10.25 (×2)	9.89 (×4), 10.02 (×2)	9.99 (×4)	shortest 13.5	shortest 13.5	10.38 (×2), 10.13, 9.93, 9.81, 9.74	9.83, 9.86, 9.88, 10.09
Interfullerene C···C contacts [Å]	3.329–3.466, –	3.276–3.410, 3.392–3.470	3.328–3.770, –	–	–	3.250–3.360	3.269–3.410

[a] The ranges for the bond lengths and angles are given for **3** and **4**. [b] The bond lengths and angles for Zn(EtMedtc)₂ are given for one of three crystallographically independent molecules.

[Cu(EtMedtc)₂]₂·C₆₀ (**11**) is isostructural to **1**. The substitution of two of four ethyl groups by methyl ones results in the decrease of the unit cell parameters of **11** relative to those of **1** (see Table 4). C₆₀ and Cu(EtMedtc)₂ molecules are ordered. Complex **11** also has a layered structure (Figure 3, a and b) with six neighbors to each C₆₀ molecule. The shortest interfullerene center-to-center distances are 9.89 (four neighbors along the diagonal to the *bc*-plane) and 10.02 Å (two neighbors in the *c*-direction; Figure 3, b). For both cases the vdW C···C contacts between adjacent fullerenes of 3.28–3.41 and 3.39–3.47 Å are shorter than 3.42 Å and center-to-center distances are close to the dis-

tance in pure C₆₀^[45] justifying the formation of closely packed hexagonal layers.

The projection of the Cu(EtMedtc)₂ layer on the C₆₀ layer is shown in Figure 3, b. The central CuS₄ fragments arranged above C₆₀ spheres allow two flexible ethyl groups to occupy cavities in the C₆₀ layers. C₆₀ forms shortened Cu···C(C₆₀) contacts of 3.334 and 3.379 Å by two carbon atoms of one 6–6 bond (Figure 3, b). VdW S, N and H···C(C₆₀) contacts are close to those in **1** and **7** (Table 2).

Cu(EtMedtc)₂ has a dimeric structure in **11** with a square pyramidal environment of Cu^{II} atoms (Figure 1) with four

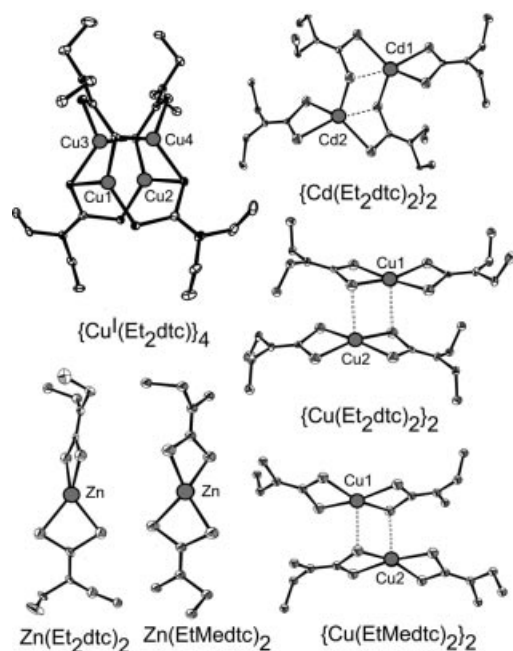


Figure 1. Molecular structures of $M(R_2dtc)_x$ in the complexes with fullerenes: $\{Cd(Et_2dtc)_2\}_2$, $\{Cu(Et_2dtc)_2\}_2$ and $\{Cu(EtMedtc)_2\}_2$ dimers; tetrahedral $Zn(Et_2dtc)_2$ and $Zn(EtMedtc)_2$ monomers and $[Cu^I(Et_2dtc)]_4$ tetramers.

short equatorial bonds (the average length is 2.325 Å) and one relatively long axial bond (2.787 Å). Both ethyl groups of $Cu(EtMedtc)_2$ are directed towards the fullerene layer.

Thus, **1**, **7**, and **11** have similar crystal structures. However, the differences in the molecular structures of $M(R_2dtc)_2$ and the length of the alkyl substituents provide their noticeable modifications. The packing motif of the fullerene layer changes from closely packed hexagonal layers in **11**, to intermediate layers in **1** (four and two neighbors with 10.02 and 10.25 Å center-to-center interfullerene distances)^[21] and finally to square layers in **7**. The character of $M(R_2dtc)_2$ -fullerene interactions also changes. Weakly bound $Cu(R_2dtc)_2$ dimers with relatively long axial bonds have a more planar shape of the $(NCS_2)_2M$ fragments than those in strongly bound $Cd(Et_2dtc)_2$ dimers with a short axial bond. The dihedral angles between the NCS_2M planes are 160.9 and 158.6° in **1** and **11**, and only 143.8° in **7** providing shorter $Cu\cdots C(C_{60})$ distances (by about 0.3 Å in **11** and **1** than the $Cd\cdots C(C_{60})$ distances in **7**. However, the more concave surface of the $Cd(Et_2dtc)_2$ fragments results in better conditions for the π - π interaction between the NCS_2Cd planes and two adjacent C_{60} hexagons (Figure 2, c) since the dihedral angle of 143.8° is close to that between adjacent C_{60} hexagons (138.5°). As a result, the NCS_2Cd planes and the C_{60} hexagons arrange parallel to each other with the dihedral angles between them equal only to 0.8 and 8.2°. High steric complementarity is probably a reason for the ability of $Cd(Et_2dtc)_2$ to quantitatively precipitate C_{60} and C_{70} complexes from solutions. More planar $Cu(R_2dtc)_2$ provides worse conditions for the π - π interac-

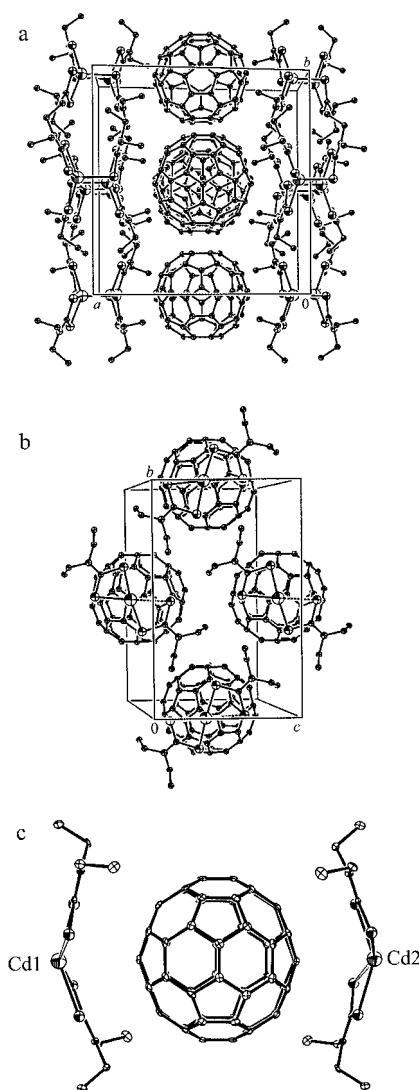


Figure 2. Crystal structure of **7**: the view of the unit cell on the ab - (a) and bc -planes (b); a mutual arrangement of concave $Cd(Et_2dtc)_2$ fragments and a spherical C_{60} molecule (c).

tions in **1** and **11** with corresponding dihedral angles of 9.8, 13.6° and 9.5, 12.6°, respectively.

$Zn(Et_2dtc)_2 \cdot C_{60} \cdot (C_6H_5Cl)_{0.5} \cdot (C_6H_6)_{0.5}$ (**6**) crystallizes in a triclinic lattice. C_{60} and $Zn(Et_2dtc)_2$ molecules are ordered, whereas C_6H_5Cl and C_6H_6 molecules share one position with equal occupancies and are disordered. Complex **6** has a unique cage structure with large channels along the a -axis accommodating $Zn(Et_2dtc)_2$ and solvent molecules. The channels are completely surrounded by the fullerene molecules, which form a hexagonal 3D framework (Figure 4). Each C_{60} molecule has six neighbors. The center-to-center distances for three of them (9.74, 9.81, and 9.93 Å) are close to that distance in pure C_{60} ,^[45] whereas the other ones are larger (10.38 Å $\times 2$ and 10.13 Å). Shortened vdW $C\cdots C$ contacts between the closest fullerenes are 3.250–3.360 Å.

$Zn(Et_2dtc)_2$ forms a complex with C_{60} in a monomeric state with nonplanar *pseudo*-tetrahedral configuration of Zn^{II} (the dihedral angle between two NCS_2Zn planes being

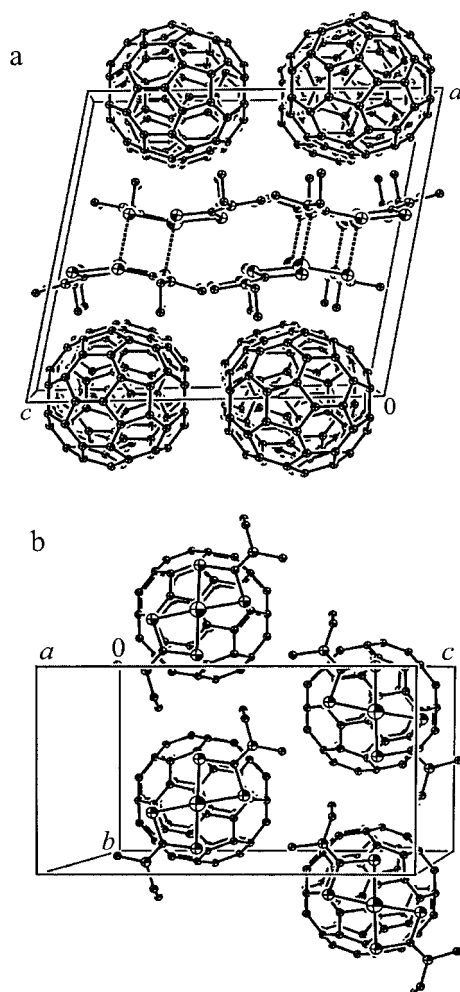


Figure 3. Crystal structure of **11**: the view of the unit cell of **11** on the *ac*- (a) and *bc*-planes (b).

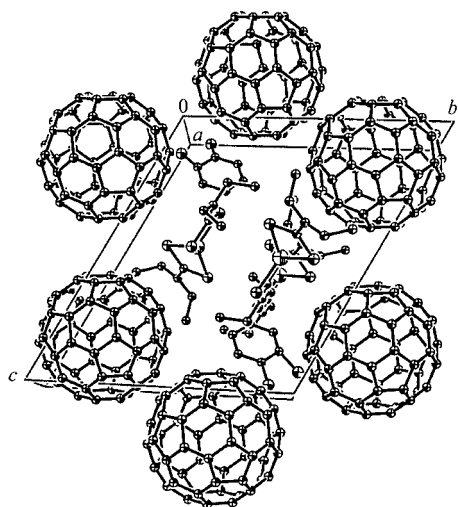


Figure 4. The view of the unit cell of **6** along the *a*-axis.

91.5°) (Figure 1). This conformation is for the first time observed for $\text{Zn}(\text{Et}_2\text{dtc})_2$. Similar geometry of the $(\text{NCS}_2)_2\text{Zn}$ fragment was reported for $\text{Zn}(\text{Bnz}_2\text{dtc})_2$ with bulky benzyl substituents,^[46] whereas pristine $\text{Zn}(\text{R}_2\text{dtc})_2$ with $\text{R} = \text{Et}$, $n\text{Pr}$, $i\text{Pr}$ substituents have dimeric structures.^[33–35]

Because of the tetrahedral geometry, only half of each $\text{Zn}(\text{Et}_2\text{dtc})_2$ molecule forms vdW contacts with C_{60} (Table 2). The closest $\text{Zn}\cdots\text{C}(\text{C}_{60})$ distances are 3.659 and 3.822 Å. The other half of the $\text{Zn}(\text{Et}_2\text{dtc})_2$ molecule locates above the adjacent $\text{Zn}(\text{Et}_2\text{dtc})_2$.

The substitution of two ethyl groups by methyl ones changes the packing motif in $[\text{Zn}(\text{EtMedtc})_2]_3 \cdot (\text{C}_{60})_2$ (**12**). In contrast to previously described complexes, both C_{60} molecules are disordered at 90 K between two orientations with 66/34 and 58/42% occupancies. These orientations are linked by the rotation of the C_{60} molecule by 180° about the axis passing through the centers of two oppositely located 5–6 bonds. There is also certain disorder in the positions of ethyl and methyl groups in $\text{Zn}(\text{EtMedtc})_2$. The complex has 3D packing of fullerenes, in which each C_{60} molecule has four neighbors and is located in the center of a distorted tetrahedron. This 3D packing can be split in strongly puckered C_{60} layers parallel to the *ac*-plane (Figure 5). Three neighbors are seen in this plane, whereas the fourth neighbor is located in the adjacent layers. The center-to-center distances are in the 9.83–10.09 Å range (the vdW radius of C_{60} is 10.18 Å) and the shortest $\text{C}\cdots\text{C}$ contacts lie in the 3.27–3.41 Å range. The cavities in the 3D framework are occupied by $\text{Zn}(\text{EtMedtc})_2$ molecules. One $\text{Zn}(\text{EtMedtc})_2$ molecule arranges parallel to the *ac*-plane and two other ones are perpendicular to this plane (Figure 5). Because of the strong puckering of fullerene layers, each $\text{Zn}(\text{EtMedtc})_2$ molecule forms vdW contacts with four fullerene ones. The $\text{Zn}\cdots\text{C}(\text{C}_{60})$ distances of 3.66–3.94 Å are similar to those in **6**.

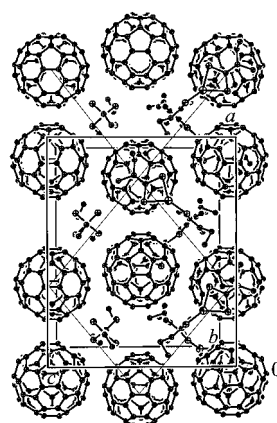


Figure 5. The view of the crystal structure of **12** on the *ac*-plane. C_{60} molecules occupy two levels. Molecules belonging to one level are connected by thin lines.

$\{[\text{Cu}^{\text{I}}(\text{Et}_2\text{dtc})_4]_4\} \cdot (\text{C}_{60})_3 \cdot (\text{C}_6\text{H}_4\text{Cl}_2)_4$ (**3**) and $\{[\text{Cu}^{\text{I}}(\text{Et}_2\text{dtc})_4]_4\} \cdot (\text{C}_{70})_3 \cdot (\text{C}_6\text{H}_4\text{Cl}_2)_4$ (**4**) are isostructural and have high-symmetry cubic unit cells with parameters of

43.7822(4) (**3**) and 44.2911(3) (**4**) Å and unusually great volumes of 83925.3(13) (**3**) and 86885.9(10) Å³ (**4**). Two symmetrically independent C₆₀ molecules are disordered. One of them is located on a twofold axis and the other molecule is on a fourfold axis. Because of the disorder, C₆₀ molecules have two and four orientations, respectively. [Cu^I(Et₂dtc)]₄ and solvent C₆H₄Cl₂ molecules are located in general positions and are ordered.

The complexes have an island motif of fullerene packing with the shortest interfullerene center-to-center distances of 13.5 Å. Loose layers can be outlined in the *bc*-plane. The main structural motif of these layers is shown in Figure 6. There are large (right in Figure 6) and small (left in Figure 6) squares consisting of five and four fullerene molecules. Each small square is surrounded by four large squares and vice versa. As this takes place, both squares have one common C₆₀ molecule. Small squares accommodate five [Cu^I(Et₂dtc)]₄ molecules, whereas large squares accommodate eight [Cu^I(Et₂dtc)]₄ and eight C₆H₄Cl₂ molecules. It is interesting that all eight C₆H₄Cl₂ molecules surround one C₆₀ molecule (Figure 6). The adjacent fullerene layers in 3D packing are arranged in such a way that large fullerene squares are located above and below small fullerene squares.

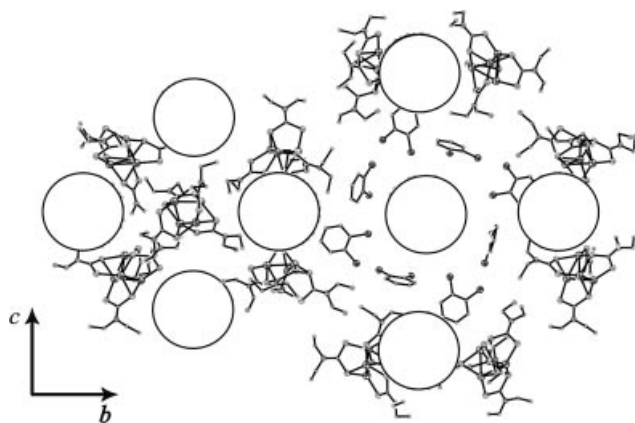


Figure 6. The view of the crystal structure of **3** on the *bc*-plane.

[Cu^I(Et₂dtc)]₄ is a tetramer containing four Cu^I(Et₂dtc) units (Figure 1). Cu^I atoms form a slightly distorted tetrahedron with the Cu...Cu distance of 2.5698(18)–2.6306(18) Å. Each Cu^I atom forms three Cu–S coordination bonds of 2.245(3)–2.281(3) Å length. Therefore, the coordination number of Cu^I is 3. Pristine Cu^I(Et₂dtc) and Au^I(Et₂dtc) form dimers,^[47,48] and for Ag^I(Et₂dtc) hexamers and polymers are also known.^[49,50] According to the best of our knowledge, a tetrameric structure is for the first time observed for Cu^I(Et₂dtc). Probably, the formation of complexes with C₆₀ and C₇₀ stabilizes the tetrameric structure. The Cu...C(C₆₀) and Cu...C(C₇₀) distances (4.80 and 4.44 Å), as well as the vdW N and S...C(fullerene) contacts (Table 2) are large enough to show low efficiency of the π - π interaction in **3** and **4**.

4. Magnetic Properties of the Complexes

EPR spectroscopy is a sensitive tool used to study changes in a local environment of Cu^{II} atoms at the formation of fullerene complexes with Cu(R₂dtc)₂. Pristine Cu(R₂dtc)₂ with R = Et, *n*Pr possess dimeric structures with square pyramidal geometry of Cu^{II} (the coordination number is 5).^[43] Such geometry is characterized by the EPR spectrum shown in part a of Figure 7. Cu(EtMedtc)₂ has an asymmetric structure and as a result shows a more asymmetric EPR signal (Supporting Information).

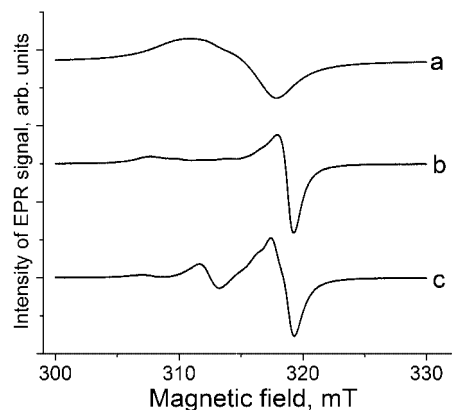


Figure 7. The EPR spectra of polycrystalline pristine Cu(Et₂dtc)₂ (a); **1** (b), and **2** (c) at 290 K.

The EPR signal of **1** (Figure 7, b) is noticeably different from that of pristine Cu(Et₂dtc)₂. According to X-ray diffraction data, Cu(Et₂dtc)₂ has a dimeric structure in **1** as well.^[21] However, noticeable changes are observed in the environment of Cu^{II}. Weak axial coordination of Cu^{II} to C₆₀ with a rather short Cu...C(C₆₀) distance of 3.27 Å enhances the asymmetry of the environment of Cu^{II}. This coordination directs oppositely to the axial Cu–S bond and results in noticeable elongation of this bond from 2.844(1) in the pristine donor to 3.030(2) Å in **1**. Consequently, the central (NCS₂)₂Cu fragments become more planar in **1** than in the pristine donor. Coordination of Cu^{II} to C₆₀ is more favorable for planar conformation of M(Et₂dtc)₂, and most probably namely this coordination evokes the flattening of the central (NCS₂)₂Cu fragments. The M...C(C₆₀) distances (3.587, 3.334, and 3.269 Å) decrease together with the flattening of M(Et₂dtc)₂ fragments in the following order: **7**, **11**, and **1** (the length of axial M–S bonds are 2.599, 2.787, and 3.030 Å, respectively).

The EPR spectra of [Cu(Et₂dtc)₂](C₇₀)₂·(C₆H₅Cl)_{0.5} (**2**, Figure 7, c), [Cu(EtMedtc)₂]₂·C₆₀ (**11**), and [Cu(*n*Pr₂dtc)₂](C₆₀)₂ (**13**) (for spectra of **11** and **13** see supporting information) are also noticeably changed relative to those of pristine Cu(R₂dtc)₂. These changes are similar to those observed in the spectrum of **1** suggesting that weak coordination of Cu^{II} to fullerenes and a flattening of the central (NCS₂)₂Cu fragments can be realized in these complexes as well.

Magnetic susceptibilities of **1** and **2** were measured from 300 down to 1.9 K and were shown to follow the Curie–Weiss law with the small negative Weiss constants of -2.5 K (**1**) and -2.0 K (**2**), which indicate only a weak antiferromagnetic interaction between Cu^{II} centers. Axial Cu–S bonds transfer the magnetic interaction in the $\{\text{Cu}(\text{Et}_2\text{dtc})_2\}_2$ dimers and their elongation at the formation of complexes with fullerenes can weaken the antiferromagnetic interaction between Cu^{II} centers.

The spectrum of C_{60} and an excess of $\text{Cu}^{\text{I}}(\text{Et}_2\text{dtc})$ in benzonitrile shows that CT is realized from donor to fullerene molecules in solution. To study CT in the solid state we measured the EPR spectra (4–290 K) and magnetic susceptibilities of $\{[\text{Cu}^{\text{I}}(\text{Et}_2\text{dtc})]_4\}_5 \cdot (\text{C}_{60})_3 \cdot (\text{C}_6\text{H}_4\text{Cl}_2)_4$ (**3**) and $\{[\text{Cu}^{\text{I}}(\text{Et}_2\text{dtc})]_4\}_5 \cdot (\text{C}_{70})_3 \cdot (\text{C}_6\text{H}_4\text{Cl}_2)_4$ (**4**) in the 2–300 K range. Pristine $\text{Cu}^{\text{I}}(\text{Et}_2\text{dtc})$ is diamagnetic and EPR silent. **3** and **4** are also diamagnetic with temperature-independent diamagnetic contributions of -0.00522 and -0.00666 emu/mol^{-1} . Paramagnetic contributions of the Curie impurities are only 0.23 and 1.3% for **3** and **4**. According to EPR at 290 K (two narrow lines with $g_1 = 2.0009$ and $g_2 = 2.0025$ for **3** and one narrow line with $g = 2.0019$ for **4**) these impurities originate mainly from defects.^[51] Thus, in spite of the observation of CT in solution, both complexes are molecular ones in the solid state. Most probably, this is associated with the formation of $[\text{Cu}^{\text{I}}(\text{Et}_2\text{dtc})]_4$ tetramers, whose shape is unfavorable for effective CT to fullerene molecules.

It is known that pristine $\text{Mn}^{\text{II}}(\text{Et}_2\text{dtc})_2$ has a polymeric structure with a distorted octahedral environment of Mn^{II} .^[39] In EPR it shows a single Lorentzian line with $g = 2.0115$ and $\Delta H = 61.8$ mT (Figure 8, a), which is characteristic of this environment of Mn^{II} .^[52] The formation of $\{\text{Mn}(\text{Et}_2\text{dtc})_2\}_2 \cdot \text{C}_{70}$ (**10**) results in considerable changes in the EPR spectrum indicating noticeable modification of the local environment of Mn^{II} . The EPR spectrum exhibits features extending from 50 to about 500 mT (Figure 8, b). Such a spectrum is typical for dinuclear Mn^{II} species^[53] and previously a very similar EPR spectrum has been observed, for example, in a dinuclear Mn^{II} complex bridged by chlorine atoms.^[54] Magnetic susceptibility data provides evidence of a strong exchange interaction between Mn^{II} cen-

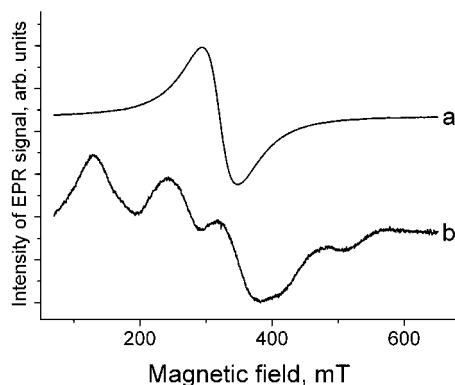


Figure 8. The EPR spectra of polycrystalline pristine $\text{Mn}(\text{Et}_2\text{dtc})_2$ (a) and polycrystalline **10** (b) at 290 K.

ters. The magnetic moment of **10** is equal to $7.78 \mu_{\text{B}}$ per formula unit at 300 K, which is close to the calculated value of $7.75 \mu_{\text{B}}$ if two $5/2$ spins contribute to magnetic susceptibility. Mn^{II} spins interact antiferromagnetically in the 150–300 K range with a large negative Weiss constant of -96 K and magnetic susceptibility decreases below 46 K (Figure 9). Such exchange interactions between Mn^{II} can be realized if $\text{Mn}(\text{Et}_2\text{dtc})_2$ forms dimers in **10** [similar to $\{\text{Cd}(\text{Et}_2\text{dtc})_2\}_2$ dimers in **7**]. EPR data support this conclusion. The EPR signal from $\text{Mn}(\text{Et}_2\text{dtc})_2$ in **10** remains unchanged qualitatively down to 4 K. No EPR signals attributed to $\text{C}_{70}^{\cdot -}$ ^[55] were found indicating the absence of CT to fullerene molecules. Thus, $\text{Mn}(\text{Et}_2\text{dtc})_2$ cannot ionize C_{70} in the solid state. Similarly, $\text{Mn}^{\text{II}}\text{TPP}$ (tetraphenylporphyrinate) ($E^{+/0}_{1/2} = -0.23$ V vs. SCE)^[56] forms only molecular complexes with fullerenes C_{60} and C_{70} .^[57]

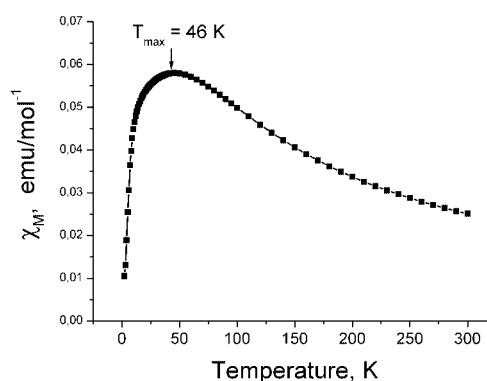


Figure 9. Molar magnetic susceptibility of polycrystalline **10** in the 1.9–300 K range.

5. IR- and UV/Visible-NIR Spectra of the Complexes

The IR spectra of **1–15** (see Supporting Information) are a superposition of those of pristine metal dithiocarbamates, fullerenes, and solvent molecules. The positions of peaks in the UV/Visible-NIR spectra of **1–15** and pristine donors are listed in Table 3. The absence of absorption in the NIR spectra of **1–15** at 1070 nm indicates neutral ground states of the complexes. Pristine $\text{Cu}(\text{Et}_2\text{dtc})_2$ has broad absorption in the visible range with the maximum at 442 nm and a shoulder at 660 nm (Figure 10, part 1, c). This absorption remains in the spectra of the complexes with the maximum at 437 nm (**1**, Figure 10, part 1, b) and 455 nm (**2**, Figure 10, part 1, a). The bands at 341 and 263 nm (**1**) and 230 nm (**2**) were ascribed to intramolecular transitions in fullerenes.^[58] The spectra of **6** (Figure 10, part 2, b) and **7** (Figure 10, part 2, a) also contain C_{60} absorption bands at 263 and 340 nm and a relatively weak band at 470 nm. The latter band ascribed to intermolecular CT between neighboring C_{60} molecules was also found in the spectra of fullerene films.^[59] A condition necessary for the observation of this band in the solid-state spectra of the complexes is close packing of fullerene molecules in the crystal.^[7,60] Since C_{60} molecules are closely packed in **1**, **7**, and **6**, this band can manifest itself in their spectra. However, in the spectrum

Table 3. UV/Vis-NIR spectra of the starting compounds and **1–15**.

Compounds	The bands of fullerenes [nm]	M[d(alkyl)dtc] _x [nm]	CT bands [nm] A (Full.)	C (D.-Full.)
C ₆₀	262 s, 341 s		470 m	
C ₇₀	–, 420 s, 540 m			
Cu(EtMedtc) ₂		267 s, 438 s, ca. 660 w		
Cu(Et ₂ dtc) ₂		271 s, 442s, ca. 660 w		
Cu(<i>n</i> Pr ₂ dtc) ₂		277 s, 449s, ca. 650 w		
Ni(<i>n</i> Pr ₂ dtc) ₂		322 s, 389 s, 606 w		
1	263 s ^[a] , 341 s	263 s ^[a] , 434 m ^[a] , ca. 650 w		–
2	383 s, 455 m ^[a]	455 m ^[a]		
3	262 s, 340 m			
4	383 s, 480 m			
5	263 s, 334 s			
6	261 s, 337 s			
7	263 s, 340 s		470 w	610 w
8	379 s, 462 m			
9	255 s, 332 s			
10	388 s, 484 m			
11	265 s ^[a] , 337 s	265 s ^[a] , 443 m ^[a] , ca. 650 w		–
12	261 s, 338 m			
13	262 s ^[a] , 341 s	262 s ^[a] , 434 m ^[a] , ca. 615 w	434 m ^[a]	900 w
14	266 s, 340 s,	ca. 605 w ^[a]	450 w	ca. 770 w ^[a]
15	266 s, 340 s		450 w	650 w

[a] The bands overlap.

of **1** it is closed by absorption of Cu(Et₂dtc)₂. A similar interfullerene CT band was reported for pristine C₇₀ at 550 nm,^[59] and it can also contribute to broad absorption of **2** at 500–600 nm (Figure 10, part 1, a).

The spectrum of **7** additionally contains a broad weak band at 610 nm (Figure 10, part 2, a). Because C₆₀ and Cd(Et₂dtc)₂ do not absorb noticeably in this range, it can be attributed to intermolecular CT from Cd(Et₂dtc)₂ to C₆₀. The observation of this band is possible due to favorable π - π interaction between Cd(Et₂dtc)₂ and C₆₀ molecules (Figure 2, c). CT bands are absent in the spectra of **6** (Figure 10, part 2, b) and **1–5**, **8–12** (Supporting Information) indicating worse conditions for the π - π interaction between nonplanar M^{II}(R₂dtc)_x and fullerenes. Absorption at 600–700 nm in the spectra of **1**, **2**, and **11** was attributed mainly to Cu(R₂dtc)₂ (a shoulder at 660 nm).

Several processes can occur at photoexcitation of **1**, **2**, and **7** in the visible range. In **1** and **2** mainly photoexcitation of Cu^{II}(Et₂dtc)₂ (437 and 660 nm) is realized together with a minor contribution of intermolecular CT between neighboring C₆₀ and C₇₀ molecules (470 and 550 nm, respectively), whereas in **7** intermolecular CT from Cd(Et₂dtc)₂ to C₆₀ molecules (610 nm) and between C₆₀ molecules (470 nm) is mainly realized.

The absorption spectra of **13** and pristine Cu(*n*Pr₂dtc)₂ are shown in part 3 of Figure 10. Additionally to absorption of Cu(*n*Pr₂dtc)₂ in the visible range (Figure 10, part 3, a, and Table 3), the intense band with the maximum at 900 nm (Figure 10, part 3, a) was attributed to CT from the Cu(*n*Pr₂dtc)₂ to the C₆₀ molecules. Similar bands are observed in the spectra of **14** and **15**. Therefore, planar M(*n*Pr₂dtc)₂ have better conditions for the π - π interaction with fullerenes than nonplanar M[(Et, Me)₂dtc]₂.

6. Photoconductivity in C₆₀ and C₇₀ Complexes with Cu(Et₂dtc)₂ and Cd(Et₂dtc)₂ (**1**, **2**, **7**, and **8**)

According to the IR- and EPR data, **1**, **2**, **7**, and **8** are molecular complexes without CT in the ground state. The crystals of **1**, **2**, and **7** have low “dark” conductivity $\sigma \approx 10^{-10}$ to 10^{-11} S·cm⁻¹. The photoexcitation of single crystals of the complexes by white light from a 150 W halogen tube with 10^{12} to 10^{14} photons/cm²·s intensity results in a 20–50-fold increase in the photocurrent in **1**, two orders of magnitude in **2**, and three orders of magnitude in **7**. These values remain unchanged under the illumination of the crystals for 10⁴ s and are completely reproducible. The crystals of **8** do not show a noticeable increase in photocurrent at photoexcitation.

Photoconductivity spectra of the complexes are shown in Figure 11. Photoconductivity has maxima at 470 nm for **1**, 450–650 nm for **2**, and about 660 nm for **7**. The comparison of the photoconductivity spectra of **1**, **2**, and **7** with their absorption spectra allows one to suppose the mechanisms of free charge carrier generation. In **1** and **2** the main contribution is given by the photoexcitation of Cu(Et₂dtc)₂ (440 and 660 nm) as well as interfullerene CT between neighboring C₆₀ or C₇₀ molecules (470 nm for **1** and 550 nm for **2**, Figure 11, a and b). The major contribution is given in **7** by CT from the Cd(Et₂dtc)₂ to the C₆₀ molecule (610 nm) with a small contribution of interfullerene CT between neighboring C₆₀ molecules (470 nm) (Figure 11, c). In spite of similar crystal structures, the mechanisms of free charge carrier generation are different in **1** and **7**. In **1** Cu(Et₂dtc)₂ has intense absorption in the visible range, whereas Cd(Et₂dtc)₂ is transparent in **7** in this range. However, steric compatibility of the Cd(Et₂dtc)₂ and C₆₀ molecules (Figure 2, c) provides better

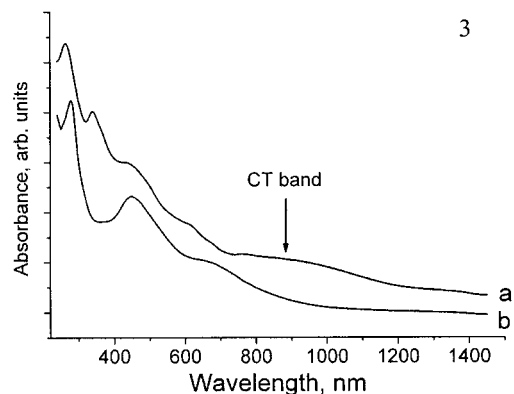
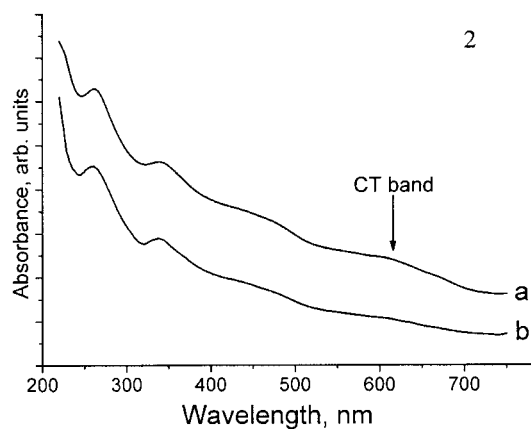
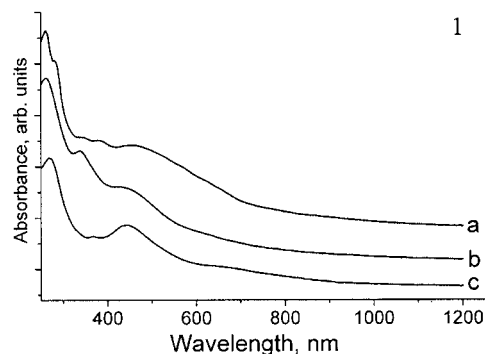


Figure 10. The UV/Visible-NIR spectra of: (1) **2** (a); **1** (b); and pristine $\text{Cu}(\text{Et}_2\text{dtc})_2$ (c). (2) **7** (a); and **6** (b). (3) **13** (a); and pristine $\text{Cu}(\text{nPr}_2\text{dtc})_2$ (b) in KBr pellets.

conditions for the π - π interaction and correspondingly for intermolecular CT in **7** than in **1**. Complex **8** has no CT band in the visible range and as a result photoconductivity was not found in this complex.

Photoconductivity of **1** and **7** is sensitive to weak magnetic field (MF) with $B_0 < 0.5$ T (Figure 12). A negative MF effect on photoconductivity is because of the reaction involving triplet CT excitons and paramagnetic centers. This interaction releases charges from deep-seated traps and increases photocurrent. A collision of triplet CT-excitons

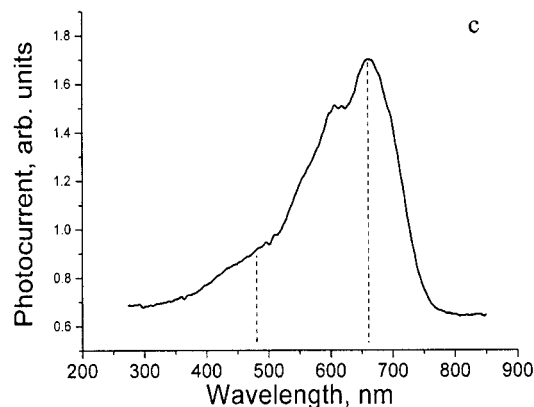
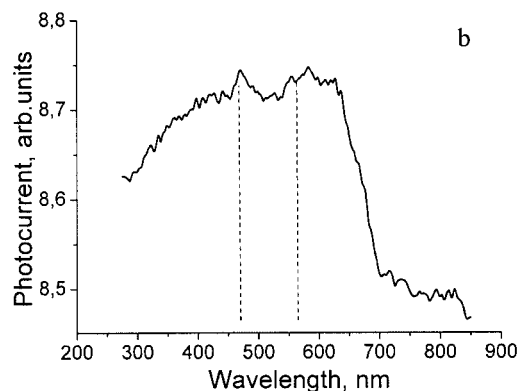
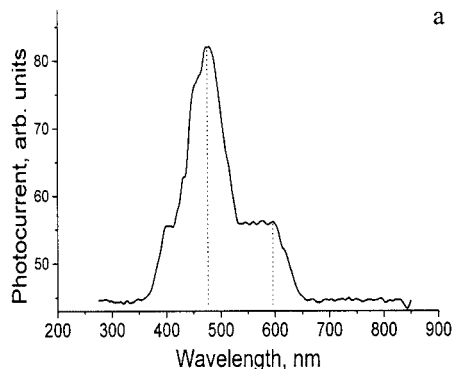
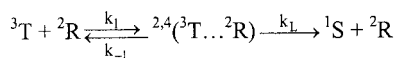


Figure 11. Photoconductivity spectra of the crystals of **1** (a), **2** (b), and **7** (c). The positions of the main peaks in the spectra are shown by dashed lines.

with doublet paramagnetic species may lead either to spin-independent triplet scattering or quenching. During quenching a transition from the initial spin state, which is a mixture of a doublet and a quartet, to a purely doublet final state takes place:



The rate constant k_L of the transition from each of the six L -th initial spin states of an intermediate complex to a final one depends on the amplitude of the doublet compo-

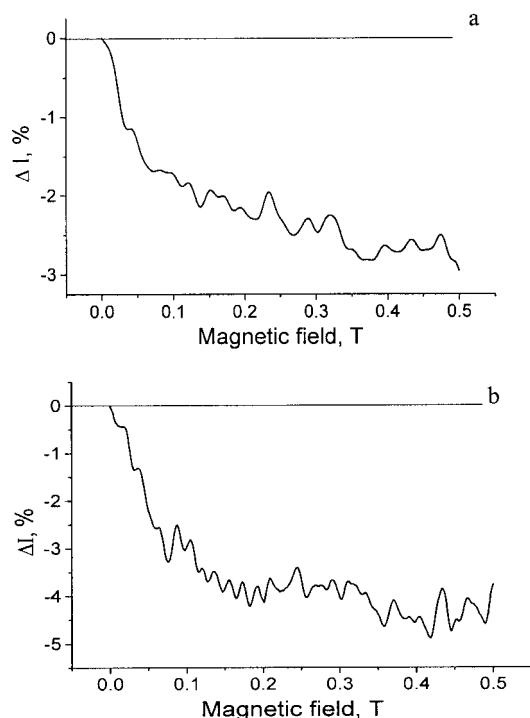


Figure 12. Magnetic field (B_0 , T) dependence of photocurrent (I , %) in **1** (a) and **7** (b).

nent therein. The total rate of exciton quenching by paramagnetic impurity is:

$$Q = \frac{1}{6} k_1 \sum_{L=1}^6 \frac{k_L}{k_1 - k_L},$$

where k_1 and k_{-1} are rate constants of collision and back scattering, respectively. The value of Q has a maximum, when a doublet component is uniformly distributed over all six substates, the minimum of Q is attained at the complete separation of a doublet and a quartet. The quenching rate is maximal in ZMF. With the application of an external MF, the doublet component concentrates on four states and the value of Q decreases together with the rate of dissociation of CT excitons and, consequently, a number of free charge carriers. A similar negative MF dependence was found in anthracene.^[61]

Conclusions

We studied the formation of the complexes between metal dialkyldithiocarbamates, $M(R_2dtc)_x$ with $R = EtMe$ (Cu^{II} , Zn^{II}); Et (Cu^{II} , Cu^I , Ag^I , Zn^{II} , Cd^{II} , Hg^{II} , Mn^{II} , Fe^{II} , Co^{II} , V^{II} , Ni^{II} , and Pt^{II}); nPr (Cu^{II} , Cu^I , Zn^{II} , Cd^{II} , Ni^{II} , and Pt^{II}) and fullerenes C_{60} and C_{70} . It was shown that $M(R_2dtc)_x$ co-crystallize with fullerenes C_{60} and C_{70} to form complexes of different structures and compositions (**1–15**). Pristine $M(R_2dtc)_x$ ($R = Et$, nPr) have a large variety of molecular structures in fullerene complexes, which can be square planar or tetrahedral monomers, strongly and weakly bound dimers and tetramers. Tetrahedral mo-

nomeric conformations for $Zn(EtMedtc)_2$ and $Zn(Et_2dtc)_2$ and tetrameric $\{Cu^I(Et_2dtc)\}_4$ were for the first time found for these metal dithiocarbamates.

Butterfly-shaped $[M\{(Me, Et)_2dtc\}_2]_2$ dimers ($M = Cu$ and Cd) form layered structures in **1**, **7**, and **11**, where the packing of C_{60} layers varies from a square to hexagonal one. The dimeric structure of dithiocarbamates provides a characteristic 1:2 composition of the complexes {Fullerene/ $M[(Et, Me)dtc]_2$ }. Complexes **8–10** have the same composition, and $M(R_2dtc)_2$ can have similar dimeric structures in these complexes. This supposition was justified for **10** by magnetic data. $Cd(Et_2dtc)_2$ has geometry conforming well to the spherical shape of fullerene molecules and shows high ability to nearly quantitatively precipitate C_{60} and C_{70} complexes from solutions. A similar ability was found for $Mn(Et_2dtc)_2$ and $Fe(Et_2dtc)_2$. Monomeric $Ni(nPr_2dtc)_2$ and $Pt(nPr_2dtc)_2$ with square planar conformation of the central $(NCS_2)_2M$ fragment form **12** and **13** with a 2:1 composition [Fullerene/ $M(nPr_2dtc)_2$]. Complexes **2** and **13** have the same composition and the formation of $Cu(Et_2dtc)_2$ and $Cu(nPr_2dtc)_2$ monomers can be supposed for these complexes as well especially because pristine $Cu(R_2dtc)_2$ can adopt a square planar conformation.^[43,44] However, X-ray diffraction data are needed to prove this supposition. Non-planar tetrahedral $Zn(EtMedtc)_2$ and $Zn(Et_2dtc)_2$ provide 3D packing of fullerenes with their tetrahedral and hexahedral arrangements. Bulky $[Cu^I(Et_2dtc)]_4$ promotes an island motif in fullerene packing.

Using $M(Et_2dtc)_x$ with different donor ability (the strongest donors contain $M = Cu^I$, Co^{II} , V^{II} , and Mn^{II}) we found that $Cu^I(R_2dtc)$, $Co(R_2dtc)_2$, and $V(R_2dtc)_2$ reduce C_{60} in benzonitrile. However, among these strong donors only fullerene complexes with $Mn(Et_2dtc)_2$ and $Cu^I(Et_2dtc)$ were obtained as crystals and no CT to fullerene molecules was found in them. The EPR spectra of paramagnetic $Cu(R_2dtc)_2$ and $Mn(Et_2dtc)_2$ noticeably change at the complex formation with fullerenes most probably due to changes in the environment of M^{II} . The EPR spectra of **1**, **2**, **11**, and **13** are noticeably modified relative to those of pristine $Cu(R_2dtc)_2$. Such changes can be a result of additional weak coordination of Cu^{II} to C_{60} and the flattening of the central $(NCS_2)_2Cu$ fragment. The changes in the EPR spectrum of $Mn(Et_2dtc)_2$ at the formation of **10** are most probably evoked by the transition from a polymeric structure of pristine $Mn(Et_2dtc)_2$ with an octahedral environment of Mn^{II} to the formation in **10** of $\{Mn(Et_2dtc)_2\}_2$ dimers, in which strong antiferromagnetic exchange interaction between Mn^{II} centers is possible.

The spectra of the complexes in the visible and NIR ranges indicate their neutral ground state. $Cu(R_2dtc)_2$ (**1**, **2**, **11**, and **13**) and $Ni(nPr_2dtc)_2$ (**14**) absorb in the visible range, whereas other $M(R_2dtc)_2$ are nearly transparent in this range. In addition to the bands associated with intramolecular transitions in fullerenes and $M(R_2dtc)_x$, the bands associated with intermolecular CT between neighboring fullerene molecules (at 470 nm for C_{60} and at 550 nm for C_{70})^[59] and CT from $M(R_2dtc)_2$ to fullerene molecules are observed. The latter CT bands are observed only in the

spectra of **7** and the complexes with planar $M(nPr_2dtc)_2$ (**13–15**). The other complexes demonstrate either weak or no CT bands indicating worse conditions for the π - π interaction between fullerenes and nonplanar $M(R_2dtc)_x$. In accordance with the neutral ground state, the crystals of **1**, **2**, and **7** show low dark conductivity of 10^{-10} to 10^{-11} S·cm $^{-1}$. The illumination of the crystals by white light with 10^{12} to 10^{14} photons/cm 2 ·s intensity results in up to a 10^3 increase in photocurrent. The photoconductivity spectra exhibit maxima at 470, 450–650, and 660 nm for **1**, **2**, and **7**, respectively. Three processes generate free charge carriers in the complexes. Photoexcitation of $Cu(Et_2dtc)_2$ contributes to photoconductivity of **1** and **2** since this donor has intense absorption in the visible range. A similar mechanism was observed in $Bz_4BTPE \cdot C_{60}$ [Bz_4BTPE : tetrabenz[1,2-bis(4*H*-thiopyran-4-ylidene)ethane}],^[62] and conjugated polymer-fullerene composites.^[63] CT from donor to fullerene molecules contributes to photoconductivity of the complexes with relatively intense CT bands in the visible-NIR range: **7** and $TBPDA \cdot (C_{60})_2$ (N,N,N',N' -tetrabenzyl-*p*-phenylenediamine).^[19] Interfullerene CT between neighboring fullerene molecules also contributes to photoconductivity in **1** and **7** as well as in pure fullerene crystals^[64] and films.^[59] Common peculiarity of the C_{60} complexes showing photoconductivity is a layered arrangement of fullerene and donor molecules in a crystal, which allow the movement of photogenerated carriers through the crystal. Weak MF with $B_0 < 0.5$ T differently affects photoconductivity of fullerene complexes. We found negative (**1** and **7**) and positive ($Bz_4BTPE \cdot C_{60}$)^[64] MF dependences as well as the field dependence with sign inversion at 0.3 T [$TBPDA \cdot (C_{60})_2$].^[19] A variety of dependences indicates that the interaction of MF with photogenerated excitons can be different in fullerene complexes depending on the donor used. The mechanisms of the effects of MF on photoconductivity involve triplet CT excitons and paramagnetic centers^[61] or the population of a triplet state from a singlet one in MF.^[65] Thus, fullerene complexes with $M\{Et_2dtc\}_2$ and other $M\{R_2dtc\}_x$ may be a new wide family of photoactive compounds. A study of the photophysical properties of these complexes is now in progress.

Experimental Section

Materials: Sodium diethyldithiocarbamate trihydrate, $[Na(Et_2dtc) \cdot 3H_2O]$, was purchased from Aldrich and recrystallized from an acetonitrile/benzene mixture. Sodium ethylmethyldithiocarbamate, $Na(EtMedtc)$, and sodium di(*n*-propyl)dithiocarbamate, $Na(nPr_2dtc)$, were obtained by the reported procedure.^[43] Carbon disulfide (3.1 mL, 0.052 mol) and sodium hydroxide (50% aqueous solution, 4 mL) were added to a stirred solution of R_2NH (0.05 mol) ($R_2NH=EtMeNH$, Aldrich, and nPr_2NH , Wako) in ethanol (5 mL) at $T < 4$ °C (ice bath). After stirring for 4–6 h at $T < 4$ °C $Na(EtMedtc)$ precipitated as white crystals. $Na(nPr_2dtc)$ was obtained by the evaporation of an ethanol/water solution without heating. Pure $Na(R_2dtc)$ were obtained by recrystallization from acetonitrile/benzene mixtures (50–80% yields). Air-sensitive $M(R_2dtc)_x$ compounds ($R = Et$, $M = Cu^I$, Co^{II} , V^{II} , Fe^{II} , and Mn^{II} ; $R = nPr$, $M = Cu^I$) were obtained by stirring anhydrous $CuCl$

(100 mg), $CoBr_2$ (150 mg), VCl_2 (100 mg), $FeBr_2$ (150 mg), and MnI_2 (150 mg) and x [$x = 1$ (Cu^I) or 2 (other metals)] molar equivalents of $Na(Et_2dtc)$ in 10 mL of degassed acetonitrile over 4 h in a glove box. $M(R_2dtc)_x$ were precipitated from acetonitrile as light yellow (Cu^I and Mn^{II}), light pink (Fe^{II}), dark green-brown (Co^{II}), and light brown (V^{II}) powders together with $NaCl(Br, I)$. The precipitates were washed with acetonitrile (3 mL) and dried. $NaCl(Br, I)$ as well as possible admixtures of unreacted $MCl(Br, I)_x$ and $Na(Et_2dtc)$ were separated from $M(R_2dtc)_x$ at a stage of complex formation with fullerene because of their insolubility in *o*-dichlorobenzene ($C_6H_4Cl_2$). Air-stable $M(R_2dtc)_2$ ($R = EtMe$, $M = Cu^{II}$, and Zn^{II} ; $R = Et$, $M = Cu^{II}$, Zn^{II} , Cd^{II} , Hg^{II} , Ag^I , Ni^{II} , and Pt^{II} ; $R = nPr$, $M = Cu^{II}$, Zn^{II} , Cd^{II} , Ni^{II} , and Pt^{II}) were obtained in aqueous solution from $CuBr_2$, $ZnCl_2$, $CdBr_2 \cdot 4H_2O$, $Hg(NO_3)_2 \cdot H_2O$, $AgNO_3$, $NiCl_2$, $PtCl_2$, and $Na(R_2dtc)$.^[43] $M(R_2dtc)_2$ were dissolved in hot chlorobenzene (C_6H_5Cl), filtered off from $NaCl$, $NaBr$, or $NaNO_3$ and the solvent was removed to dryness on a rotary evaporator to yield pure $M(R_2dtc)_2$ with satisfactory elemental analyses (50–80% yield). C_{60} of 99.98% purity and C_{70} of 99.0% purity were used from MTR Ltd. Solvents were purified under argon. $C_6H_4Cl_2$ and C_6H_5Cl were distilled over CaH_2 . Hexane and benzonitrile (C_6H_5CN) were distilled over $Na/benzophenone$. For the synthesis of air-sensitive $M(R_2dtc)_x$ ($R = Et$, $M = Cu^I$, Co^{II} , V^{II} , Fe^{II} , and Mn^{II} ; $R = nPr$, $M = Cu^I$) and the preparation of the fullerene complexes, solvents were degassed and stored in a MBraun 150B-G glove box with a controlled atmosphere with contents of H_2O and O_2 of less than 1 ppm. The crystals of **3**, **4**, and **10** were stored in a glove box and were sealed in 2-mm quartz tubes for EPR and SQUID measurements under 10^{-5} Torr. KBr pellets for IR- and UV/Visible-NIR measurements were prepared in a glove box.

Synthesis: The composition of **1–5**, **7–11**, and **13–15** was determined from the elemental analysis (Table 1) and was justified for **1**, **3**, **4**, **6**, **7**, **11**, and **12** by X-ray diffraction on a single crystal.

The crystals of **1**, **2**, **5**, **6**, **9**, and **11–15** were obtained by a slow evaporation of chlorobenzene solution (15 mL) containing C_{60} (25 mg, 0.0347 mmol) and two molar equivalents of $M(R_2dtc)_x$ (0.06940 mmol) over 1 week. The crystals precipitated were washed with an excess of acetone (50–80% yield). The shapes of the crystals are presented in Table 1.

The crystals of **3** and **4** were obtained under anaerobic conditions by a slow diffusion of hexane (20 mL) in $C_6H_4Cl_2$ solution (20 mL) containing C_{60} (25 mg, 0.0347 mmol) (**3**) or C_{70} (20 mg, 0.0238 mmol) (**4**) and a fourfold molar excess of $Cu^I(Et_2dtc)$ in a glass tube of 45 mL volume with a ground glass plug. After 1 month large black prisms of **3** and **4** were precipitated on the wall of the tube (up to $0.5 \times 0.5 \times 0.8$ mm 3 size). The solvent was decanted and the crystals were washed with hexane (50–60% yield).

$Cd(Et_2dtc)_2$, $Mn(Et_2dtc)_2$, and $Fe(Et_2dtc)_2$ nearly quantitatively precipitate C_{60} and C_{70} from different solvents (C_6H_6 , C_6H_5Cl , and $C_6H_4Cl_2$). Because of this, the crystals of **7** and **8** were obtained by the diffusion of a benzene solution (20 mL) of C_{60} (20 mg, 0.02775 mmol) (**7**) or C_{70} (20 mg, 0.0238 mmol) (**8**) in $CHCl_3$ solution (20 mL) containing a twofold molar excess of $Cd(Et_2dtc)_2$. The crystals precipitated on the wall of the tube after 1 month. They were washed with acetone (70–90% yield).

The crystals of **10** were obtained similarly under anaerobic conditions by the diffusion of benzene solution (20 mL) of C_{70} (20 mg, 0.0238 mmol) (**8**) into $C_6H_4Cl_2$ containing a twofold molar excess of $Mn(Et_2dtc)_2$. The crystals precipitated on the wall of the tube after 1 month. They were washed with hexane (70% yield).

Table 4. X-ray diffraction data for **1**, **3**, **4**, **6**, **7**, **11**, and **12**.

	1 ^[21]	3	4
Structural formula	[Cu(Et ₂ dtc) ₂] ₂ ·C ₆₀	{[Cu ^I (Et ₂ dtc) ₄] ₄ } ₅ ·(C ₆₀) ₃ ·(C ₆ H ₄ Cl ₂) ₄	{[Cu ^I (Et ₂ dtc) ₄] ₄ } ₅ ·(C ₇₀) ₃ ·(C ₆ H ₄ Cl ₂) ₄
Empirical formula	C ₈₀ H ₄₀ Cu ₂ N ₄ S ₈	C ₇₆ H ₅₄ Cl ₂ Cu ₅ N ₅ S ₁₀	C _{83.50} H ₅₄ Cl ₂ Cu ₅ N ₅ S ₁₀
<i>M_r</i> [g·mol ⁻¹]	1440.72	1746.41	1836.52
Crystal shape and color	black hexagonal prisms	black cubes	black cubes
Size [mm×mm×mm]	0.40×0.30×0.25	0.50×0.40×0.40	0.40×0.30×0.30
Crystal system	monoclinic	cubic	cubic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pn</i> 3̄ <i>n</i>	<i>Pn</i> 3̄ <i>n</i>
<i>a</i> [Å]	16.1948(8)	43.7822(4)	44.2911(3)
<i>b</i> [Å]	10.2552(5)	43.7822(4)	44.2911(3)
<i>c</i> [Å]	17.2192(9)	43.7822(4)	44.2911(3)
<i>α</i> [°]	90	90	90
<i>β</i> [°]	102.504(2)	90	90
<i>γ</i> [°]	90	90	90
<i>V</i> [Å ³]	2791.9(2)	83925.3(13)	86885.9(10)
<i>Z</i>	2	48	48
<i>ρ</i> _{calc} [g/cm ³]	1.714	1.655	1.685
<i>μ</i> [mm ⁻¹]	1.12	1.921	1.860
<i>F</i> (000)	1468	42240	44592
Absorption correction	no correction	no correction	SADABS ^[66]
Max./min. transmission	0.77/0.66	0.51/0.45	0.60/0.52
<i>T</i> [K]	90(2)	90(2)	90(1)
Max. 2 θ [°]	54.12	50.04	50.04
Reflections measured	25977	524031	690665
Unique reflections	5683	12379	12798
<i>R</i> _{int}	0.036	0.0429	0.0637
Parameters, restraints	425, 0	450, 0	458, 0
Reflections [<i>F</i> _o > 2σ(<i>F</i> _o)]	4983	9398	8774
<i>R</i> ₁ [<i>F</i> _o > 2σ(<i>F</i> _o)]	0.0404	0.0984	0.0935
<i>wR</i> ₂ (all data) ^[a]	0.1064	0.2904	0.3181
<i>a</i>	0.0341	0.1060	0.1330
<i>b</i>	8.2311	2219.48	2964.08
<i>G.O.F.</i>	1.082	1.132	1.054
Restr. <i>G.O.F.</i>	1.082	1.132	1.054
CCDC number	260289	286142	286143
	6	7	11
Structural formula	Zn(Et ₂ dtc) ₂ ·C ₆₀ ·(C ₆ H ₅ Cl) _{0.5} ·(C ₆ H ₆) _{0.5}	[Cd(Et ₂ dtc) ₂] ₂ ·C ₆₀	[Cu(EtMedtc) ₂] ₂ ·C ₆₀
Empirical formula	C ₇₆ H _{25.5} Cl _{0.5} N ₂ S ₄ Zn	C ₈₀ H ₄₀ Cd ₂ N ₄ S ₈	C ₇₆ H ₃₂ Cu ₂ N ₄ S ₈
<i>M_r</i> [g·mol ⁻¹]	1177.82	1538.44	1384.62
Crystal shape and color	black parallelepipeds	brown rhombus	black rhombus
Size [mm×mm×mm]	0.33×0.20×0.20	0.40×0.30×0.10	0.42×0.38×0.10
Crystal system	triclinic	monoclinic	monoclinic
Space group	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁
<i>a</i> [Å]	10.3762(5)	16.1712(13)	16.0626(4)
<i>b</i> [Å]	15.1717(7)	16.9680(12)	10.0196(3)
<i>c</i> [Å]	17.0002(8)	10.5355(8)	17.0653(5)
<i>α</i> [°]	115.893(1)	90	90
<i>β</i> [°]	91.555(1)	99.857(2)	100.9490(13)
<i>γ</i> [°]	102.938(1)	90	90
<i>V</i> [Å ³]	2322.53(19)	2848.2(4)	2696.51(13)
<i>Z</i>	2	2	2
<i>ρ</i> _{calc} [g/cm ³]	1.684	1.794	1.705
<i>μ</i> [mm ⁻¹]	0.797	1.098	1.156
<i>F</i> (000)	1196	1544	1404
Absorption correction	SADABS ^[66]	SADABS ^[66]	no correction
Max./min. transmission	0.86/0.78	0.90/0.72	0.89/0.64
<i>T</i> [K]	90(1)	123(2)	100(2)
Max. 2 θ [°]	58.0	51.88	54.96
Reflections measured	25011	13023	20222
Unique reflections	7276	3602	11660
<i>R</i> _{int}	0.03	0.0333	
Parameters, restraints	724, 10	424, 423	812, 0
Reflections [<i>F</i> _o > 2σ(<i>F</i> _o)]	6312	3100	10282
<i>R</i> ₁ [<i>F</i> _o > 2σ(<i>F</i> _o)]	0.042	0.0358	0.0381
<i>wR</i> ₂ (all data) ^[a]	0.1177	0.085	0.0902
<i>a</i>	0.0582	0.040	0.0294
<i>b</i>	5.0135	5.096	3.4011
<i>G.O.F.</i>	1.042	1.055	1.033
Restr. <i>G.O.F.</i>	1.056	1.006	1.033
CCDC number	286144	288291	288292
	12		
Structural formula	[Zn(EtMedtc) ₂] ₃ ·(C ₆₀) ₂		
Empirical formula	C ₁₄₄ H ₅₄ N ₆ S ₁₂ Zn ₃		
<i>M_r</i> [g·mol ⁻¹]	2442.71		
Crystal shape and color	black rhombus		
Size [mm×mm×mm]	0.40×0.30×0.20		
Crystal system	orthorhombic		
Space group	<i>Pn</i> 2 ₁ / <i>a</i>		
<i>a</i> [Å]	20.815(5)		
<i>b</i> [Å]	26.072(6)		
<i>c</i> [Å]	17.128(4)		
<i>α</i> [°]	90		
<i>β</i> [°]	90		
<i>γ</i> [°]	90		
<i>V</i> [Å ³]	9298.88(12)		
<i>Z</i>	4		
<i>ρ</i> _{calc} [g/cm ³]	1.746		
<i>μ</i> [mm ⁻¹]	1.109		
<i>F</i> (000)	4944		
Absorption correction	no correction		
Max./min. transmission	0.81/0.66		
<i>T</i> [K]	100(2)		
Max. 2 θ [°]	51.48		
Reflections measured	42780		
Unique reflections	17592		
<i>R</i> _{int}			
Parameters, restraints	2393, 11252		
Reflections [<i>F</i> _o > 2σ(<i>F</i> _o)]	8450		
<i>R</i> ₁ [<i>F</i> _o > 2σ(<i>F</i> _o)]	0.1038		
<i>wR</i> ₂ (all data) ^[a]	0.3023		
<i>a</i>	0.1956		
<i>b</i>	0.0000		
<i>G.O.F.</i>	0.954		
Restr. <i>G.O.F.</i>	0.758		
CCDC number	288293		

[a] (a) $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

The C_{60} complexes with $Mn(Et_2dtc)_2$ and $Fe(Et_2dtc)_2$ were also obtained as powders by mixing C_{60} (25 mg, 0.0347 mmol) and a twofold molar excess of $M(Et_2dtc)_2$ in $C_6H_4Cl_2$ (20 mL) on heating (60 °C, 2 h). The hot solution was filtered, cooled down to room temperature, and stood overnight. The solution became colorless, and a light brown polycrystalline precipitate was formed. However, in contrast to crystals of **10**, powdered samples did not show reasonable elemental analyses probably because of the high air-sensitivity of the complexes. Indeed, $Mn(Et_2dtc)_2$ and $Fe(Et_2dtc)_2$ are extremely air-sensitive and oxidize in a few seconds in air.

We tried to crystallize the C_{60} complexes with $Co(Et_2dtc)_2$ and $V(Et_2dtc)_2$. C_{60} (25 mg, 0.0347 mmol) and a twofold molar excess of $M(Et_2dtc)_2$ were dissolved in $C_6H_4Cl_2$ (20 mL) on stirring at 60 °C for 4 h. The hot solution was filtered, cooled down to room temperature, and filtered in a glass tube of 45 mL volume with a ground glass plug. Slow diffusion of hexane (20 mL) was carried out under anaerobic conditions. However, only black powder without crystals formed after 2 months.

General: UV/Visible-NIR spectra were measured with a Shimadzu-3100 spectrometer in the 240–2600 nm range. FT-IR spectra were measured in KBr pellets with a Perkin–Elmer 1000 Series spectrometer (400–7800 cm^{-1}). A Quantum Design MPMS-XL SQUID magnetometer was used to measure static magnetic susceptibilities of **1–4** and **10** from 1.9 up to 300 K. A sample holder contribution and core temperature independent diamagnetic susceptibility (χ_0) were subtracted from the experimental values. The values of Θ , χ_0 were calculated using the appropriate formula: $\chi_M = C/(T - \Theta) + \chi_0$. EPR spectra were recorded for **1**, **2**, **11**, and **13** at room temp. and for **3**, **4**, and **10** from RT down to 4 K with a JEOL JES-TE 200 X-band ESR spectrometer equipped with a JEOL ES-CT470 cryostat. Photoconductivity of **1**, **2**, **7**, and **8** was excited using a white light halogen tube with 10^{12} – 10^{14} photons/ cm^2 s intensity. To record the spectra of photoconductivity the light beam of a xenon lamp was transmitted through a high-aperture monochromator. A static magnetic field with the induction up to 1 T was generated by an electromagnet of a Radiopan SE/X 2547 ESR spectrometer.

X-ray Crystal Structure Determination: X-ray diffraction data for **1**, **3**, **4**, **6**, **7**, **11**, and **12** were collected with a Bruker SMART1000 CCD diffractometer installed at a rotating anode source (Mo- K_α radiation, $\lambda = 0.71073$ Å), and equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. The data were collected by the rotation method with 0.3° frame-width (ω scan) and 10 s exposure time per frame. Four sets of data (600 frames in each set) were collected, nominally covering half of the reciprocal space. The data were integrated, scaled, sorted and averaged using the SMART software package.^[66] The structures were solved by the direct methods using SHELXTL NT Version 5.10.^[67] The structure was refined by full-matrix least-squares against F^2 . The details of the X-ray crystal structure analysis for **1**, **3**, **4**, **6**, **7**, **11**, and **12** including CCDC numbers for the structures are given in Table 4. Non-hydrogen atoms were refined in the anisotropic approximation. Positions of hydrogen atoms were calculated geometrically. Subsequently, the positions of H-atoms were refined by the “riding” model with $U_{iso} = 1.2U_{eq}$ of the connected non-hydrogen atom or as ideal CH_3 groups with $U_{iso} = 1.5U_{eq}$. The supplementary crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (for details see the footnote on the first page of this article): IR-data, UV/Vis-NIR spectra of pristine donors and complexes **1–15**, and EPR spectra of pristine Cu-

(EtMedtc)₂ and Cu(*n*Pr₂dtc)₂ and complexes **11** and **13** (Tables S1 and S2, Figures S1–S7).

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