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# 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 *n*Pr

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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<sup>II</sup> (C<sub>60</sub>, 1; C<sub>70</sub>, 2), Cu<sup>I</sup> (C<sub>60</sub>, 3; C<sub>70</sub>, 4), Ag<sup>I</sup> (C<sub>60</sub>, 5), Zn<sup>II</sup> (C<sub>60</sub>, **6**), Cd<sup>II</sup> (C<sub>60</sub>, **7**; C<sub>70</sub>, **8**), Hg<sup>II</sup> (C<sub>60</sub>, **9**), Mn<sup>II</sup> (C<sub>70</sub>, **10**)], R = Et and Me  $[M = Cu^{II} (C_{60}, 11), and Zn^{II} (C_{60}, 12)], and R = nPr [M =$  $Cu^{II}$  (C<sub>60</sub>, **13**), Ni<sup>II</sup> (C<sub>60</sub>, **14**), and Pt<sup>II</sup> (C<sub>60</sub>, **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<sup>II</sup> and Mn<sup>II</sup>. The EPR spectra of 1, 2, 11, and 13 are essentially modified relative to those of pristine Cu(R<sub>2</sub>dtc)<sub>2</sub> because of a weak coordination of Cu<sup>II</sup> to fullerene

#### Introduction

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

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Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author. and a flattening of the central (NCS<sub>2</sub>)<sub>2</sub>Cu 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<sub>2</sub>dtc)<sub>2</sub>]<sub>2</sub> dimers in **10**. The illumination of the crystals of **1**, **2**, and **7** by white light results in up to a 10<sup>3</sup> 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<sub>2</sub>dtc)<sub>2</sub> in **1** and **2**, and by charge transfer from Cd(Et<sub>2</sub>dtc)<sub>2</sub> to C<sub>60</sub> 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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porphyrins and metalloporphyrins,<sup>[9-11]</sup> porphyrazines,<sup>[12]</sup> metallocenes,<sup>[13–17]</sup> and others.<sup>[6]</sup> Great interest in fullerene complexes was evoked by their intriguing properties. Ionic compounds show ferromagnetism<sup>[5]</sup> and reversibly form  $\sigma$ bonded structures.<sup>[15–17]</sup> Neutral complexes were also used as templates for the preparation of fullerene polymers.<sup>[18]</sup> They can manifest photoconductivity<sup>[19]</sup> and excited ionic states upon photoexcitation by white light.<sup>[20]</sup> 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<sub>2</sub>dtc)<sub>2</sub>, co-crystallizes with fullerenes to form a molecular complex,  $[Cu(Et_2dtc)_2]_2 \cdot C_{60}$ , with a layered structure.<sup>[21]</sup> This work was extended to metal(II) dithiocarbamates with bulkier benzyl (abbreviation: substituents Bnz), namely, Cu(Bnz<sub>2</sub>dtc)<sub>2</sub>, Ni(Bnz<sub>2</sub>dtc)<sub>2</sub>, Pd(Bnz<sub>2</sub>dtc)<sub>2</sub>, and Pt(Bnz<sub>2</sub>dtc)<sub>2</sub>. They co-crystallize with  $C_{60}$  to form  $M(Bnz_2dtc)_2$ .  $C_{60}$  ( $C_6H_5Cl$ )<sub>0.5</sub> complexes.<sup>[22]</sup> In contrast to dimeric Cu(dedtc)<sub>2</sub>, M(Bnz<sub>2</sub>dtc)<sub>2</sub> are monomers with planar conformation of the central (NCS<sub>2</sub>)<sub>2</sub>M fragment, which is charac-



teristic of Ni<sup>II</sup>, Pd<sup>II</sup>, and Pt<sup>II</sup> dithiocarbamates.<sup>[23–27]</sup> Moreover, Pd(Bnz<sub>2</sub>dtc)<sub>2</sub> forms a multi-component ionic complex containing C<sub>60</sub> and bis(benzene)chromium ion-radicals: [Cr<sup>I</sup>(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>.<sup>+</sup>]·(C<sub>60</sub><sup>-</sup>)·[Pd(Bnz<sub>2</sub>dtc)<sub>2</sub>]<sub>0.5</sub>. The complex demonstrates unusual low-temperature dimerization of C<sub>60</sub><sup>-</sup> with a relatively large hysteresis and the decrease of the dimerization temperature at a fast cooling rate.<sup>[22]</sup> Thus, metal dialkyldithiocarbamates, M(R<sub>2</sub>dtc)<sub>x</sub>, 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(R<sub>2</sub>dtc)<sub>x</sub> for a long time, their donor-acceptor complexes with  $\pi$ -acceptors are rare. To our knowledge, only some complexes of molybdenum and tungsten dialkyldithiocarbamates with tetracyanoquinodimethane were described.<sup>[28,29]</sup>

 $M(R_2dtc)_x$  can easily be modified. It is possible to vary molecular structures of  $M(R_2dtc)_x$  by changing "M" or the length of alkyl substituents (R). Donor properties of  $M(R_2dtc)_x$  can also be varied from weak donors to strong ones<sup>[30]</sup> potentially able to ionize fullerenes. Some of  $M(R_2dtc)_x$  have broad absorption in the visible range or outstanding magnetic properties [for example, Fe<sup>III</sup>-(Et<sub>2</sub>dtc)<sub>2</sub>Cl is the first single-component ferromagnet with  $T_c = 2.46 \text{ K}]^{[31]}$  and, therefore, they can be used as light harvesting or magnetic components for the complexes.

In the present work we studied the effect of  $M(R_2dtc)_x$ (depending on M and R) on composition, structure, electronic, and physical properties of their complexes with fullerenes. We used monomeric, dimeric, and tetrameric  $M(R_2dtc)_x$  and varied the length of alkyl (R) substituents (Me, Et, and *n*Pr).  $M(R_2dtc)_x$  were both weak and strong donors. The interaction of  $C_{60}$  with the strongest donors (Cu<sup>I</sup>, Mn<sup>II</sup>, Co<sup>II</sup>, and V<sup>II</sup> diethyldithiocarbamates) was studied in benzonitrile solution. Fifteen complexes of C<sub>60</sub> and C70 with Cu<sup>II</sup>, Cu<sup>I</sup>, Ag<sup>I</sup>, Zn<sup>II</sup>, Cd<sup>II</sup>, Hg<sup>II</sup>, Mn<sup>II</sup>, Ni<sup>II</sup>, and Pt<sup>II</sup> 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  $M(R_2dtc)_x$  (M = Cu<sup>I</sup>, Cu<sup>II</sup>, and Mn<sup>II</sup>) were investigated by SQUID and EPR techniques. Photoconductivity of single crystals of four C<sub>60</sub> and C<sub>70</sub> complexes with  $Cu(Et_2dtc)_2$  and  $Cd(Et_2dtc)_2$  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  $M(Et_2dtc)_2$  donors (M = Cu<sup>I</sup>, Mn<sup>II</sup>, Co<sup>II</sup>, and V<sup>II</sup>) with C<sub>60</sub> was studied in solution.

 $C_{60}$  and a fivefold molar excess of the corresponding  $M(Et_2dtc)_x$  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<sup>I</sup>, Co<sup>II</sup>, and V<sup>II</sup> diethyldithiocarbamates reduce  $C_{60}$  to a radical anion, and an absorption band characteristic of  $C_{60}^-$  is manifested at 1070 nm. On the contrary,  $Mn(Et_2dtc)_2$  cannot reduce  $C_{60}$ . These observations are in agreement with redox potentials of metal(II) dithiocarbamates. Related octahedral  $M^{III}$ -(dtc)<sub>3</sub><sup>1-/0</sup> ( $M^{3+}/M^{2+}$  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).<sup>[30]</sup>  $C_{60}$  has the first  $E^{0/-}$  potential at –0.485 V(vs. Ag/AgCl).<sup>[32]</sup>

#### 2. Synthesis of Solid Complexes

The complexes obtained and the data from the elemental analysis are listed in Table 1. The ability of  $M(R_2dtc)_x$  to co-crystallize with  $C_{60}$  and  $C_{70}$  as well as the composition of the complexes depend on the metal (M) and the length of the alkyl substituents (R). Pristine  $M(R_2dtc)_2$  (R = Et, *n*Pr) have different conformations of the central (NCS<sub>2</sub>)<sub>2</sub>M fragment. Ni(R<sub>2</sub>dtc)<sub>2</sub> and Pt(R<sub>2</sub>dtc)<sub>2</sub> have square planar conformation.<sup>[23–27]</sup> Zn(R<sub>2</sub>dtc)<sub>2</sub>,<sup>[33–35]</sup> Cd(R<sub>2</sub>dtc)<sub>2</sub>,<sup>[36,37]</sup> and Fe(Et<sub>2</sub>dtc)<sub>2</sub><sup>[38]</sup> are dimers with a tetrahedral environment of M<sup>II</sup>. Mn(Et<sub>2</sub>dtc)<sub>2</sub> is a polymer with an octahedral environment of Mn<sup>II,[39]</sup> Hg(R<sub>2</sub>dtc)<sub>2</sub><sup>[40–42]</sup> and Cu(R<sub>2</sub>dtc)<sub>2</sub><sup>[43]</sup> have both square planar or square pyramidal dimeric conformations.

 $M(Et_2dtc)_2$  (M = Cd<sup>II</sup>, Hg<sup>II</sup>, and Mn<sup>II</sup>) co-crystallize with fullerenes in dimeric conformation to form 1:2 [C<sub>60</sub>/ M(R<sub>2</sub>dtc)<sub>2</sub>] complexes. As this takes place, Cd(Et<sub>2</sub>dtc)<sub>2</sub>, and Mn(Et<sub>2</sub>dtc)<sub>2</sub> precipitate C<sub>60</sub> and C<sub>70</sub> complexes from C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>5</sub>Cl, and C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> solutions in nearly a quantitative yield [a similar ability was found for Fe(Et<sub>2</sub>dtc)<sub>2</sub>]. On the contrary, square planar Ni(Et<sub>2</sub>dtc)<sub>2</sub>, and Pt(Et<sub>2</sub>dtc)<sub>2</sub> or Co-(Et<sub>2</sub>dtc)<sub>2</sub> and V(Et<sub>2</sub>dtc)<sub>2</sub>, which reduce C<sub>60</sub> in solution, do not form crystals of the complexes with fullerenes.

Elongation of alkyl substituents in  $M(nPr_2dtc)_2$  drastically changes their complex formation with fullerenes. Ni $(nPr_2dtc)_2$  and Pt $(nPr_2dtc)_2$  with square planar conformation form 2:1 [C<sub>60</sub>/M $(nPr_2dtc)_2$ ] complexes with C<sub>60</sub>. Similarly, among different metal(II) dibenzyldithiocarbamates only Ni(Bnz<sub>2</sub>dtc)<sub>2</sub>, Pd(Bnz<sub>2</sub>dtc)<sub>2</sub>, and Pt(Bnz<sub>2</sub>dtc)<sub>2</sub> with the same conformation co-crystallize with C<sub>60</sub>.<sup>[22]</sup> It is interesting to note that Cu(R<sub>2</sub>dtc)<sub>2</sub> form 1:2, 2:1, and 1:1 [C<sub>60</sub>:Cu(R<sub>2</sub>dtc)<sub>2</sub>] complexes independently of the R (MeEt, Et, *n*Pr, and Bnz) length. It seems possible that Cu(R<sub>2</sub>dtc)<sub>2</sub> in the complexes with fullerenes can adopt both square planar<sup>[43,44]</sup> and square pyramidal dimeric conformations.<sup>[43]</sup>

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  $M(R_2dtc)_x$  and  $Cd(Et_2dtc)_2$ .

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

		Elemental	l analysis fo	und/calcd.				Color and shape
		C [%]	H [%]	N [%]	Cl [%]	S [%]	M [%]	
$[Cu(Et_2dtc)_2]_2 \cdot C_{60}^{[a]} [21]$	1	66.46	3.08	4.10	0			black hexagonal
		66.70	2.77	3.88	0	17.77	8.88	plates
$[Cu(Et_2dtc)_2] \cdot (C_{70})_2 \cdot (C_6H_5Cl)_{0.5}$	2	83.54	2.24	1.75	0.91			black prisms
		83.51	1.42	1.77	1.12	8.12	4.06	*
${[Cu^{I}(Et_{2}dtc)]_{4}}_{5} \cdot (C_{60})_{3} \cdot (C_{6}H_{4}Cl_{2})_{4}^{[a]}$	3	51.71	3.11	3.75	5.58			black prisms
		50.75	3.19	4.14	4.21	18.93	18.78	*
$\{[Cu^{I}(Et_{2}dtc)]_{4}\}_{5} \cdot (C_{70})_{3} \cdot (C_{6}H_{4}Cl_{2})_{4}^{[a]}$	4	53.68	2.97	3.50	4.64			black prisms
		53.26	3.03	3.93	3.93	17.97	17.83	*
$Ag^{I}(Et_{2}dtc) \cdot C_{60} \cdot C_{6}H_{6}$	5	82.14	1.48	1.33	_			black prisms
		80.85	1.52	1.32	_	6.07	10.24	*
$Zn(Et_2dtc)_2 \cdot C_{60} \cdot (C_6H_5Cl)_{0.5} \cdot (C_6H_6)_{0.5}^{[a]}$	6	According	g to X-ray d	liffraction d	lata			brown prisms
$\{Cd(Et_2dtc)_2\}_2 \cdot C_{60}^{[a]}$	7	61.02	3.04	3.79	_			red-brown rhombus
		61.50	2.67	3.73	_	17.09	15.01	
$\{Cd(Et_2dtc)_2\}_2 \cdot C_{70}$	8	64.41	3.32	3.38	< 0.7			red-brown rhombus
		65.20	2.41	3.33	0	15.45	13.57	
$\{Hg(Et_2dtc)_2\}_2 \cdot C_{60}$	9	56.00	2.35	3.37	_			black hexagonal
		55.02	2.39	3.34	_	15.29	23.96	plates
$\{Mn(Et_2dtc)_2\}_2 \cdot C_{70}$	10	68.88 <sup>[b]</sup>	2.59	3.69	0			black elongated
								parallelepipeds
		70.05	2.98	3.63	0	16.60	7.13	
$[Cu(EtMedtc)_2]_2 \cdot C_{60}^{[a]}$	11	66.13	2.21	4.01	_			black rhombus
		65.92	2.31	4.04	_	18.49	9.24	
$[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2^{[a]}$	12	According	g to X-ray d	liffraction d	lata			black rhombus
$[Cu(nPr_2dtc)_2] \cdot (C_{60})_2$	13	86.74	1.48	1.44	0			thin needles
		86.67	1.51	1.51	0	6.89	3.42	
$[Ni(nPr_2dtc)_2] \cdot (C_{60})_2$	14	87.01	1.50	1.47	0			thin needles
		86.91	1.50	1.50	0	6.88	3.21	
$[Pt(nPr_2dtc)_2] \cdot (C_{60})_2$	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  $Mn(Et_2dtc)_2$ .

#### 3. Crystal Structures

Main geometric parameters of  $M(R_2dtc)_x$  and van der Waals (vdW) contacts in the complexes with fullerenes are listed in Table 2. Molecular structures of  $M(R_2dtc)_x$  are shown in Figure 1.

The crystal structure of  $[Cu(Et_2dtc)_2]_2{\boldsymbol{\cdot}}C_{60}$  (1) has been described previously.^{[21]}

[Cd(Et<sub>2</sub>dtc)<sub>2</sub>]<sub>2</sub>·C<sub>60</sub> (7) has a crystal structure similar to that of 1. Cd(Et<sub>2</sub>dtc)<sub>2</sub> and C<sub>60</sub> molecules are ordered at 120 K. Complex 7 has a layered structure (Figure 2, parts a and b), in which layers of closely packed C<sub>60</sub> molecules alternate with those composed of Cd(Et<sub>2</sub>dtc)<sub>2</sub> dimers. Each C<sub>60</sub> 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 C<sub>60</sub> crystals at 153 K (9.94 Å).<sup>[45]</sup> The vdW C···C contacts are 3.33–3.77 Å. Two other neighboring fullerenes are arranged in the *c*-direction with a centerto-center distance of 10.54 Å (longer than the vdW diameter of C<sub>60</sub> molecules of 10.18 Å). Therefore, C<sub>60</sub> molecules have a square arrangement in the layers.

The projection of the  $Cd(Et_2dtc)_2$  layer on the  $C_{60}$  one is shown in part b of Figure 2. The central  $CdS_4$  fragments

are arranged strictly above the  $C_{60}$  spheres, whereas flexible ethyl substituents occupy available cavities in the  $C_{60}$  layers. The effective packing of  $Cd(Et_2dtc)_2$  and  $C_{60}$  molecules in a crystal is attained due to a butterfly shape of  $Cd(Et_2dtc)_2$ dimers (Figure 1), which allows them to encapsulate  $C_{60}$ molecules (Figure 2, c).

The packing of Cd(Et<sub>2</sub>dtc)<sub>2</sub> dimers in the layer has a parquet-like motif (Figure 2, b). The shortest  $Cd \cdots C(C_{60})$  contacts of 3.587 and 3.592 Å are formed with two carbon atoms of the 6-6 bond of C<sub>60</sub>. These contacts are noticeably longer than the Cu···C(C<sub>60</sub>) contacts in 1 (3.334 and 3.379 Å).<sup>[21]</sup> Co-crystallization of Cd(Et<sub>2</sub>dtc)<sub>2</sub> with C<sub>60</sub> does not affect its geometry. The pristine donor has a dimeric structure with a nearly tetrahedral environment of Cd<sup>II</sup> 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).<sup>[36]</sup> The dimeric structure of Cd(Et<sub>2</sub>dtc)<sub>2</sub> 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  $Cd(Et_2dtc)_2$  are directed towards the fullerene layer in 7 (Figure 2, c), whereas in 1 three of four ethyl groups of Cu(Et<sub>2</sub>dtc)<sub>2</sub> are directed towards the fullerene layer.<sup>[21]</sup>

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



Complex	1	11	7	3	4	6	12
Geometry	Dimer	Dimer	Dimer	Tetramer <sup>[a]</sup>	Tetramer <sup>[a]</sup>	Tetrahedral monomer	Tetrahedral monomer <sup>[b]</sup>
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	tetrahedron	_	_
				2.5855(17)-	2.5698(18)-		
				2.6239(17)	2.6306(18)		
		Donor–Fu	illerene interactions	s, shortest vdW co	ntacts		
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-Fullerer	ne interaction			
Packing of	hexagonal	hexagonal	square layers,	isolated	isolated	hexagonal, 3D,	tetragonal, 3D,
fullerenes	layers,	layers,	4 neighbors			6 neighbors	4 neighbors
	6 neighbors	6 neighbors					
Interfullerene	10.02 (×4),	9.89 (×4),	9.99 (×4)	shortest 13.5	shortest 13.5	10.38 (×2),	9.83, 9.86,
center-to-center	10.25 (×2)	10.02 (×2)				10.13, 9.93,	9.88, 10.09
distances [Å]						9.81, 9.74	-
Interfullerene C····C	3.329-3.466	3.276-3.410.	3.328-3.770	_	_	3.250-3.360	3.269-3.410
contacts [Å]	_	3.392-3.470	_				

[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.

 $[Cu(EtMedtc)_{2]_{2}} \cdot C_{60}$  (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).  $C_{60}$  and  $Cu(EtMedtc)_{2}$  molecules are ordered. Complex 11 also has a layered structure (Figure 3, a and b) with six neighbors to each  $C_{60}$  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  ${\rm C_{60}}^{[45]}$  justifying the formation of closely packed hexagonal layers.

The projection of the Cu(EtMedtc)<sub>2</sub> layer on the C<sub>60</sub> layer is shown in Figure 3, b. The central CuS<sub>4</sub> fragments arranged above C<sub>60</sub> spheres allow two flexible ethyl groups to occupy cavities in the C<sub>60</sub> layers. C<sub>60</sub> forms shortened Cu···C(C<sub>60</sub>) 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(C<sub>60</sub>) 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  $Cu^{\rm II}$  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)<sub>2</sub> 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)<sup>[21]</sup> and finally to square layers in 7. The character of M(R<sub>2</sub>dtc)<sub>2</sub>-fullerene interactions also changes. Weakly bound Cu(R<sub>2</sub>dtc)<sub>2</sub> dimers with relatively long axial bonds have a more planar shape of the  $(NCS_2)_2M$  fragments than those in strongly bound Cd(Et<sub>2</sub>dtc)<sub>2</sub> dimers with a short axial bond. The dihedral angles between the NCS<sub>2</sub>M planes are 160.9 and 158.6° in 1 and 11, and only 143.8° in 7 providing shorter Cu···C(C<sub>60</sub>) 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<sub>2</sub>dtc)<sub>2</sub> fragments results in better conditions for the  $\pi$ - $\pi$  interaction between the NCS<sub>2</sub>Cd planes and two adjacent C<sub>60</sub> hexagons (Figure 2, c) since the dihedral angle of 143.8° is close to that between adjacent C<sub>60</sub> hexagons (138.5°). As a result, the NCS<sub>2</sub>Cd planes and the C<sub>60</sub> 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<sub>60</sub> and C<sub>70</sub> complexes from solutions. More planar  $Cu(R_2dtc)_2$  provides worse conditions for the  $\pi$ - $\pi$  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<sub>60</sub> molecule (c).

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

Zn(Et<sub>2</sub>dtc)<sub>2</sub>·C<sub>60</sub>·(C<sub>6</sub>H<sub>5</sub>Cl)<sub>0.5</sub>·(C<sub>6</sub>H<sub>6</sub>)<sub>0.5</sub> (**6**) crystallizes in a triclinic lattice. C<sub>60</sub> and Zn(Et<sub>2</sub>dtc)<sub>2</sub> molecules are ordered, whereas C<sub>6</sub>H<sub>5</sub>Cl and C<sub>6</sub>H<sub>6</sub> 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<sub>2</sub>dtc)<sub>2</sub> and solvent molecules. The channels are completely surrounded by the fullerene molecules, which form a hexagonal 3D framework (Figure 4). Each C<sub>60</sub> 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<sub>60</sub>.<sup>[45]</sup> whereas the other ones are larger (10.38 Å ×2 and 10.13 Å). Shortened vdW C···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<sub>2</sub>Zn planes being



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

91.5°) (Figure 1). This conformation is for the first time observed for  $Zn(Et_2dtc)_2$ . Similar geometry of the  $(NCS_2)_2Zn$  fragment was reported for  $Zn(Bnz_2dtc)_2$  with bulky benzyl substituents,<sup>[46]</sup> whereas pristine  $Zn(R_2dtc)_2$  with R = Et, *n*Pr, *i*Pr substituents have dimeric structures.<sup>[33–35]</sup>

Because of the tetrahedral geometry, only half of each  $Zn(Et_2dtc)_2$  molecule forms vdW contacts with  $C_{60}$  (Table 2). The closest  $Zn\cdots C(C_{60})$  distances are 3.659 and 3.822 Å. The other half of the  $Zn(Et_2dtc)_2$  molecule locates above the adjacent  $Zn(Et_2dtc)_2$ .

The substitution of two ethyl groups by methyl ones changes the packing motif in  $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$  (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 Zn(EtMedtc)<sub>2</sub>. The complex has 3D packing of fullerenes, in which each C<sub>60</sub> molecule has four neighbors and is located in the center of a distorted tetrahedron. This 3D packing can be split in strongly puckered C<sub>60</sub> 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 centerto-center distances are in the 9.83-10.09 Å range (the vdW radius of  $C_{60}$  is 10.18 Å) and the shortest C···C contacts lie in the 3.27-3.41 Å range. The cavities in the 3D framework are occupied by Zn(EtMedtc)<sub>2</sub> molecules. One Zn-(EtMedtc)<sub>2</sub> 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 Zn(EtMedtc)<sub>2</sub> molecule forms vdW contacts with four fullerene ones. The Zn···C(C<sub>60</sub>) distances of 3.66–3.94 Å are similar to those in 6.



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



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.

 ${[Cu^{I}(Et_{2}dtc)]_{4}}_{5} \cdot (C_{60})_{3} \cdot (C_{6}H_{4}Cl_{2})_{4}$  (3) and  ${[Cu^{I}-(Et_{2}dtc)]_{4}}_{5} \cdot (C_{70})_{3} \cdot (C_{6}H_{4}Cl_{2})_{4}$  (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) Å (4). Two symmetrically independent  $C_{60}$  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,  $C_{60}$  molecules have two and four orientations, respectively.  $[Cu^{I}(Et_{2}dtc)]_{4}$  and solvent  $C_{6}H_{4}Cl_{2}$  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 C<sub>60</sub> molecule. Small squares accommodate five [Cu<sup>I</sup>(Et<sub>2</sub>dtc)]<sub>4</sub> molecules, whereas large squares accommodate eight  $[Cu^{I}(Et_{2}dtc)]_{4}$  and eight  $C_{6}H_{4}Cl_{2}$  molecules. It is interesting that all eight C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> molecules surround one  $C_{60}$  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<sup>I</sup>(Et<sub>2</sub>dtc)]<sub>4</sub> is a tetramer containing four Cu<sup>I</sup>(Et<sub>2</sub>dtc) units (Figure 1). Cu<sup>I</sup> atoms form a slightly distorted tetrahedron with the Cu···Cu distance of 2.5698(18)– 2.6306(18) Å. Each Cu<sup>I</sup> atom forms three Cu–S coordination bonds of 2.245(3)–2.281(3) Å length. Therefore, the coordination number of Cu<sup>I</sup> is 3. Pristine Cu<sup>I</sup>(Et<sub>2</sub>dtc) and Au<sup>I</sup>(Et<sub>2</sub>dtc) form dimers,<sup>[47,48]</sup> and for Ag<sup>I</sup>(Et<sub>2</sub>dtc) hexamers and polymers are also known.<sup>[49,50]</sup> According to the best of our knowledge, a tetrameric structure is for the first time observed for Cu<sup>I</sup>(Et<sub>2</sub>dtc). Probably, the formation of complexes with C<sub>60</sub> and C<sub>70</sub> stabilizes the tetrameric structure. The Cu···C(C<sub>60</sub>) and Cu···C(C<sub>70</sub>) 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  $\pi$ - $\pi$  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  $Cu(R_2dtc)_2$ . Pristine  $Cu(R_2dtc)_2$  with R = Et, *n*Pr possess dimeric structures with square pyramidal geometry of  $Cu^{II}$  (the coordination number is 5).<sup>[43]</sup> 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  $Cu(Et_2dtc)_2$  (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(Et<sub>2</sub>dtc)<sub>2</sub>. According to X-ray diffraction data, Cu(Et<sub>2</sub>dtc)<sub>2</sub> has a dimeric structure in 1 as well.<sup>[21]</sup> However, noticeable changes are observed in the environment of Cu<sup>II</sup>. Weak axial coordination of Cu<sup>II</sup> to  $C_{60}$  with a rather short Cu···C( $C_{60}$ ) distance of 3.27 Å enhances the asymmetry of the environment of Cu<sup>II</sup>. 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 (NCS<sub>2</sub>)<sub>2</sub>Cu fragments become more planar in 1 than in the pristine donor. Coordination of Cu<sup>II</sup> to C<sub>60</sub> is more favorable for planar conformation of M(Et<sub>2</sub>dtc)<sub>2</sub>, and most probably namely this coordination evokes the flattening of the central (NCS<sub>2</sub>)<sub>2</sub>Cu fragments. The M···C(C<sub>60</sub>) distances (3.587, 3.334, and 3.269 Å) decrease together with the flattening of  $M(Et_2dtc)_2$  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  $[Cu(Et_2dtc)_2] \cdot (C_{70})_2 \cdot (C_6H_5Cl)_{0.5}$  (2, Figure 7, c),  $[Cu(EtMedtc)_2]_2 \cdot C_{60}$  (11), and  $[Cu(nPr_2dtc)_2] \cdot (C_{60})_2$  (13) (for spectra of 11 and 13 see supporting information) are also noticeably changed relative to those of pristine  $Cu(R_2dtc)_2$ . 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 (NCS<sub>2</sub>)<sub>2</sub>Cu 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<sup>II</sup> centers. Axial Cu–S bonds transfer the magnetic interaction in the {Cu-(Et<sub>2</sub>dtc)<sub>2</sub>}<sub>2</sub> dimers and their elongation at the formation of complexes with fullerenes can weaken the antiferromagnetic interaction between Cu<sup>II</sup> centers.

The spectrum of  $C_{60}$  and an excess of  $Cu^{I}(Et_{2}dtc)$  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  $\{[Cu^{I}(Et_{2}dtc)]_{4}\}_{5} \cdot (C_{60})_{3} \cdot (C_{6}H_{4}Cl_{2})_{4}$  (3) and  ${[Cu^{I}(Et_{2}dtc)]_{4}}_{5} \cdot (C_{70})_{3} \cdot (C_{6}H_{4}Cl_{2})_{4}$  (4) in the 2–300 K range. Pristine Cu<sup>I</sup>(Et<sub>2</sub>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<sup>-1</sup>. 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.<sup>[51]</sup> 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  $[Cu^{I}(Et_{2}dtc)]_{4}$  tetramers, whose shape is unfavorable for effective CT to fullerene molecules.

It is known that pristine  $Mn^{II}(Et_2dtc)_2$  has a polymeric structure with a distorted octahedral environment of  $Mn^{II}$ .<sup>[39]</sup> 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  $Mn^{II}$ .<sup>[52]</sup> The formation of  $\{Mn(Et_2dtc)_2\}_2 \cdot C_{70}$  (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<sup>[53]</sup> and previously a very similar EPR spectrum has been observed, for example, in a dinuclear  $Mn^{II}$  complex bridged by chlorine atoms.<sup>[54]</sup> Magnetic susceptibility data provides evidence of a strong exchange interaction between  $Mn^{II}$  cen-



Figure 8. The EPR spectra of polycrystalline pristine  $Mn(Et_2dtc)_2$  (a) and polycrystalline **10** (b) at 290 K.

ters. The magnetic moment of 10 is equal to 7.78  $\mu_B$  per formula unit at 300 K, which is close to the calculated value of 7.75  $\mu_B$  if two 5/2 spins contribute to magnetic susceptibility. Mn<sup>II</sup> 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<sup>II</sup> can be realized if Mn(Et<sub>2</sub>dtc)<sub>2</sub> forms dimers in 10 [similar to  $\{Cd(Et_2dtc)_2\}_2$  dimers in 7]. EPR data support this conclusion. The EPR signal from Mn(Et<sub>2</sub>dtc)<sub>2</sub> in 10 remains unchanged qualitatively down to 4 K. No EPR signals attributed to  $C_{70}$  [55] were found indicating the absence of CT to fullerene molecules. Thus,  $Mn(Et_2dtc)_2$  cannot ionize  $C_{70}$ in the solid state. Similarly, Mn<sup>II</sup>TPP (tetraphenylporphyrinate)  $(E^{+/0}_{1/2} = -0.23 \text{ V vs. SCE})^{[56]}$  forms only molecular complexes with fullerenes  $C_{60}$  and  $C_{70}$ .<sup>[57]</sup>



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 Cu(Et<sub>2</sub>dtc)<sub>2</sub> 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 retains 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.<sup>[58]</sup> 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<sub>60</sub> molecules was also found in the spectra of fullerene films.<sup>[59]</sup> 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.<sup>[7,60]</sup> Since  $C_{60}$ molecules are closely packed in 1, 7, and 6, this band can manifest itself in their spectra. However, in the spectrum

Compounds	The bands of fullerenes [nm]	$M[d(alkyl)dtc]_x$ [nm]	CT bands [nm] A (Full.)	C (DFull.)
Céo	262 s. 341 s		470 m	<u> </u>
C <sub>70</sub>	- 420 s 540 m			
$Cu(EtMedtc)_2$	, . <u>2</u> 0 3, 0 10 III	267 s. 438 s. ca. 660 w		
$Cu(Et_{a}dt_{c})_{a}$		271  s 442  s ca $660  w$		
$Cu(nPr_{e}dt_{c})_{2}$		277  s, 449  s, ca. 650  w		
Ni( <i>n</i> Prodtc) <sub>2</sub>		322 s 389 s 606 w		
1	263 s <sup>[a]</sup> 341 s	$263 \text{ s}^{[a]} 434 \text{ m}^{[a]} ca 650 \text{ w}$		_
2	$383 \le 455 m^{[a]}$	$455 \text{ m}^{[a]}$		
2	262 s 340 m	+55 m <sup>-</sup>		
J 1	202 S, 540 m			
4 5	263 a 224 a			
5 6	205 8, 554 8			
0	201 8, 337 8		470	(10
/	203 8, 340 8		470 W	610 W
8	379 s, 462 m			
9	255 s, 332 s			
10	388 s, 484 m	· · · · ·		
11	265 s <sup>[a]</sup> , 337 s	265 s <sup>[a]</sup> , 443 m <sup>[a]</sup> , ca. 650 w		_
12	261 s, 338 m			
13	262 s <sup>[a]</sup> , 341 s	262 s <sup>[a]</sup> , 434 m, <sup>[a]</sup> ca. 615 w	434 m <sup>[a]</sup>	900 w
14	266 s, 340 s,	ca. 605 w <sup>[a]</sup>	450 w	ca. 770 w <sup>[a]</sup>
15	266 s, 340 s		450 w	650 w

Table 3. U	UV/Vis-NIR	spectra of	f the	starting	compounds	and	1-1	15.
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[a] The bands overlap.

of **1** it is closed by absorption of  $Cu(Et_2dtc)_2$ . A similar interfullerene CT band was reported for pristine  $C_{70}$  at 550 nm,<sup>[59]</sup> 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  $C_{60}$  and  $Cd(Et_2dtc)_2$  do not absorb noticeably in this range, it can be attributed to intermolecular CT from  $Cd(Et_2dtc)_2$  to  $C_{60}$ . The observation of this band is possible due to favorable  $\pi$ - $\pi$  interaction between  $Cd(Et_2dtc)_2$  and  $C_{60}$  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  $\pi$ - $\pi$  interaction between nonplanar  $M^{II}(R_2dtc)_x$  and fullerenes. Absorption at 600– 700 nm in the spectra of **1**, **2**, and **11** was attributed mainly to  $Cu(R_2dtc)_2$  (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  $Cu^{II}(Et_2dtc)_2$  (437 and 660 nm) is realized together with a minor contribution of intermolecular CT between neighboring  $C_{60}$  and  $C_{70}$  molecules (470 and 550 nm, respectively), whereas in 7 intermolecular CT from  $Cd(Et_2dtc)_2$  to  $C_{60}$  molecules (610 nm) and between  $C_{60}$  molecules (470 nm) is mainly realized.

The absorption spectra of **13** and pristine  $Cu(nPr_2dtc)_2$ are shown in part 3 of Figure 10. Additionally to absorption of  $Cu(nPr_2dtc)_2$  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  $Cu(nPr_2dtc)_2$  to the  $C_{60}$  molecules. Similar bands are observed in the spectra of **14** and **15**. Therefore, planar  $M(nPr_2dtc)_2$  have better conditions for the  $\pi$ - $\pi$  interaction with fullerenes than nonplanar M[(Et, Me)\_2dtc]\_2.

# 6. Photoconductivity in $C_{60}$ and $C_{70}$ Complexes with $Cu(Et_2dtc)_2$ and $Cd(Et_2dtc)_2$ (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<sup>-1</sup>. The photoexcitation of single crystals of the complexes by white light from a 150 W halogen tube with  $10^{12}$  to  $10^{14}$  photons/cm<sup>2</sup>·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  $10^4$  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(Et<sub>2</sub>dtc)<sub>2</sub> (440 and 660 nm) as well as interfullerene CT between neighboring  $C_{60}$  or  $C_{70}$  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  $Cd(Et_2dtc)_2$  to the  $C_{60}$  molecule (610 nm) with a small contribution of interfullerene CT between neighboring C<sub>60</sub> 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  $Cu(Et_2dtc)_2$  has intense absorption in the visible range, whereas Cd(Et<sub>2</sub>dtc)<sub>2</sub> is transparent in 7 in this range. However, steric compatibility of the Cd(Et<sub>2</sub>dtc)<sub>2</sub> and C<sub>60</sub> molecules (Figure 2, c) provides better





Figure 10. The UV/Visible-NIR spectra of: (1) 2 (a); 1 (b); and pristine  $Cu(Et_2dtc)_2$  (c). (2) 7 (a); and 6 (b). (3) 13 (a); and pristine  $Cu(nPr_2dtc)_2$  (b) in KBr pellets.

conditions for the  $\pi$ - $\pi$  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 spinindependent 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:

$${}^{3}T + {}^{2}R \xrightarrow{k_{1}} {}^{2,4}({}^{3}T \dots {}^{2}R) \xrightarrow{k_{L}} {}^{1}S + {}^{2}R$$

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.<sup>[61]</sup>

#### Conclusions

We studied the formation of the complexes between metal dialkyldithiocarbamates,  $M(R_2dtc)_x$  with R = EtMe $(Cu^{II}, Zn^{II})$ ; Et  $(Cu^{II}, Cu^{I}, Ag^{I}, Zn^{II}, Cd^{II}, Hg^{II}, Mn^{II}, Fe^{II}, Co^{II}, V^{II}, Ni^{II}, and Pt^{II})$ ; *n*Pr  $(Cu^{II}, Cu^{I}, Zn^{II}, Cd^{II}, Ni^{II}, and Pt^{II})$  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, *n*Pr) 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 monomeric 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<sub>60</sub> 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<sub>2</sub>dtc)<sub>2</sub> has geometry conforming well to the spherical shape of fullerene molecules and shows high ability to nearly quantitatively precipitate C<sub>60</sub> and C<sub>70</sub> 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<sub>2</sub>)<sub>2</sub>M fragment form 12 and 13 with a 2:1 composition [Fullerene/M( $nPr_2dtc$ )<sub>2</sub>]. 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.<sup>[43,44]</sup> However, X-ray diffraction data are needed to prove this supposition. Nonplanar tetrahedral Zn(EtMedtc)<sub>2</sub> and Zn(Et<sub>2</sub>dtc)<sub>2</sub> provide 3D packing of fullerenes with their tetrahedral and hexahedral arrangements. Bulky [Cu<sup>I</sup>(Et<sub>2</sub>dtc)]<sub>4</sub> promotes an island motif in fullerene packing.

Using  $M(Et_2dtc)_x$  with different donor ability (the strongest donors contain M = Cu<sup>I</sup>, Co<sup>II</sup>, V<sup>II</sup>, and Mn<sup>II</sup>) we found that  $Cu^{I}(R_{2}dtc)$ ,  $Co(R_{2}dtc)_{2}$ , and  $V(R_{2}dtc)_{2}$  reduce C<sub>60</sub> 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<sup>II</sup>. The EPR spectra of 1, 2, 11, and 13 are noticeably modified relative to those of pristine Cu(R<sub>2</sub>dtc)<sub>2</sub>. Such changes can be a result of additional weak coordination of  $Cu^{II}$  to  $C_{60}$  and the flattening of the central (NCS<sub>2</sub>)<sub>2</sub>Cu 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<sub>2</sub>dtc)<sub>2</sub> 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<sup>II</sup> centers is possible.

The spectra of the complexes in the visible and NIR ranges indicate their neutral ground state. Cu(R<sub>2</sub>dtc)<sub>2</sub> (1, 2, 11, and 13) and Ni(*n*Pr<sub>2</sub>dtc)<sub>2</sub> (14) absorb in the visible range, whereas other M(R<sub>2</sub>dtc)<sub>2</sub> are nearly transparent in this range. In addition to the bands associated with intramolecular transitions in fullerenes and M(R<sub>2</sub>dtc)<sub>x</sub>, the bands associated with intermolecular CT between neighboring fullerene molecules (at 470 nm for C<sub>60</sub> and at 550 nm for C<sub>70</sub>)<sup>[59]</sup> and CT from M(R<sub>2</sub>dtc)<sub>2</sub> 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  $\pi$ - $\pi$  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<sup>-1</sup>. The illumination of the crystals by white light with  $10^{12}$  to 10<sup>14</sup> photons/cm<sup>2</sup>·s intensity results in up to a 10<sup>3</sup> 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<sub>2</sub>dtc)<sub>2</sub> contributes to photoconductivity of 1 and 2 since this donor has intense absorption in the visible range. A similar mechanism was observed in Bz<sub>4</sub>BTPE·C<sub>60</sub> {Bz<sub>4</sub>BTPE: tetrabenzo[1,2bis(4H-thiopyran-4-ylidene)ethane]},<sup>[62]</sup> and conjugated polymer-fullerene composites.<sup>[63]</sup> 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·(C<sub>60</sub>)<sub>2</sub> (N,N,N', N'-tetrabenzyl-pphenylenediamine).<sup>[19]</sup> Interfullerene CT between neighboring fullerene molecules also contributes to photoconductivity in 1 and 7 as well as in pure fullerene crystals<sup>[64]</sup> and films.<sup>[59]</sup> Common peculiarity of the C<sub>60</sub> 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· $(C_{60})_2$ ].<sup>[19]</sup> 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<sup>[61]</sup> or the population of a triplet state from a singlet one in MF.<sup>[65]</sup> 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(Et2dtc)· 3H<sub>2</sub>O], was purchased from Aldrich and recrystallized from an acetonitrile/benzene mixture. Sodium ethylmethyldithiocarbamate, and di(n-propyl)dithiocarbamate, Na(EtMedtc). sodium Na(nPr<sub>2</sub>dtc), were obtained by the reported procedure.<sup>[43]</sup> Carbon disulfide (3.1 mL, 0.052 mol) and sodium hydroxide (50 % aqueous solution, 4 mL) were added to a stirred solution of R<sub>2</sub>NH (0.05 mol) (R<sub>2</sub>NH=EtMeNH, Aldrich, and nPr<sub>2</sub>NH, 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<sub>2</sub>dtc) was obtained by the evaporation of an ethanol/water solution without heating. Pure Na(R<sub>2</sub>dtc) were obtained by recrystallization from acetonitrile/benzene mixtures (50-80% yields). Air-sensitive  $M(R_2dtc)_x$  compounds (R = Et, M = Cu<sup>I</sup>, Co<sup>II</sup>, V<sup>II</sup>, Fe<sup>II</sup>, and Mn<sup>II</sup>; R = nPr,  $M = Cu^{I}$ ) were obtained by stirring anhydrous CuCl

(100 mg), CoBr<sub>2</sub> (150 mg), VCl<sub>2</sub> (100 mg), FeBr<sub>2</sub> (150 mg), and  $MnI_2$  (150 mg) and x [x = 1 (Cu<sup>I</sup>) or 2 (other metals)] molar equivalents of Na(Et<sub>2</sub>dtc) in 10 mL of degassed acetonitrile over 4 h in a glove box.  $M(R_2dtc)_x$  were precipitated from acetonitrile as light yellow (CuI and MnII), light pink (FeII), dark green-brown (CoII), and light brown (VII) 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)<sub>x</sub> and Na(Et<sub>2</sub>dtc) were separated from  $M(R_2dtc)_x$  at a stage of complex formation with fullerene because of their insolubility in odichlorobenzene (C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>). Air-stable M(R<sub>2</sub>dtc)<sub>2</sub> (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<sup>II</sup>; R = nPr, M = Cu<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup>, Ni<sup>II</sup>, and Pt<sup>II</sup>) were obtained in aqueous solution from CuBr<sub>2</sub>, ZnCl<sub>2</sub>, CdBr<sub>2</sub>·4H<sub>2</sub>O, Hg(NO<sub>3</sub>)<sub>2</sub>· H<sub>2</sub>O, AgNO<sub>3</sub>, NiCl<sub>2</sub>, PtCl<sub>2</sub>, and Na(R<sub>2</sub>dtc).<sup>[43]</sup> M(R<sub>2</sub>dtc)<sub>2</sub> were dissolved in hot chlorobenzene (C<sub>6</sub>H<sub>5</sub>Cl), filtered off from NaCl, NaBr, or NaNO<sub>3</sub> and the solvent was removed to dryness on a rotary evaporator to yield pure M(R<sub>2</sub>dtc)<sub>2</sub> 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<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>Cl were distilled over CaH<sub>2</sub>. Hexane and benzonitrile (C6H5CN) were distilled over Na/benzophenone. For the synthesis of air-sensitive  $M(R_2dtc)_x$  (R = Et, M = Cu<sup>I</sup>, Co<sup>II</sup>,  $V^{II}$ , Fe<sup>II</sup>, and Mn<sup>II</sup>; R = *n*Pr, M = Cu<sup>I</sup>) 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<sub>2</sub>O and O<sub>2</sub> 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<sup>-5</sup> 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<sub>60</sub> (25 mg, 0.0347 mmol) and two molar equivalents of M(R<sub>2</sub>dtc)<sub>x</sub> (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<sup>3</sup> size). The solvent was decanted and the crystals were washed with hexane (50–60% yield).

Cd(Et<sub>2</sub>dtc)<sub>2</sub>, Mn(Et<sub>2</sub>dtc)<sub>2</sub>, and Fe(Et<sub>2</sub>dtc)<sub>2</sub> nearly quantitatively precipitate C<sub>60</sub> and C<sub>70</sub> from different solvents (C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>5</sub>Cl, and C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>). Because of this, the crystals of **7** and **8** were obtained by the diffusion of a benzene solution (20 mL) of C<sub>60</sub> (20 mg, 0.02775 mmol) (**7**) or C<sub>70</sub> (20 mg, 0.0238 mmol) (**8**) in CHCl<sub>3</sub> solution (20 mL) containing a twofold molar excess of Cd(Et<sub>2</sub>dtc)<sub>2</sub>. 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<sub>2</sub>dtc)<sub>2</sub>. 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.

	<b>1</b> <sup>[21]</sup>	3	4	
Structural formula	[Cu(Etadtc)a]a:Cca	$\{[Cu^{I}(Et_{2}dt_{C})]_{\ell}\}_{\epsilon}$	{[Cu <sup>I</sup> (Et_dtc)]_}_{c'(C_{70})}	). (C.H.Cl.)
Empirical formula	$C_{89}H_{49}C_{119}N_4S_9$	$C_{72}H_{54}C_{12}C_{115}N_{5}S_{10}$	Con coHeaClaClieNeSu	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
M [g·mol <sup>-1</sup> ]	1440 72	1746 41	1836 52	1
Crystal shape and color	hlack hexagonal prisms	black cubes	black cubes	
Size [mm×mm×mm]	$0.40 \times 0.20 \times 0.25$	$0.50 \times 0.40 \times 0.40$	$0.40 \times 0.20 \times 0.20$	
Size [iiiii^iiiii^iiii]	$0.40 \times 0.50 \times 0.25$	0.30 ~ 0.40 ~ 0.40	$0.40 \times 0.50 \times 0.50$	
Crystal system	monoclinic		cubic	
Space group	$P2_1/c$	Pn3n	Pn3n	
	16.1948(8)	43.7822(4)	44.2911(3)	
b [Å]	10.2552(5)	43.7822(4)	44.2911(3)	
c [A]	17.2192(9)	43.7822(4)	44.2911(3)	
a [°]	90	90	90	
β [°]	102.504(2)	90	90	
γ [°]	90	90	90	
V [Å <sup>3</sup> ]	2791.9(2)	83925.3(13)	86885.9(10)	
Ζ	2	48	48	
$\rho_{\rm calc}  [\rm g/cm^3]$	1.714	1.655	1.685	
$\mu [\mathrm{mm}^{-1}]$	1.12	1.921	1.860	
F(000)	1468	42240	44592	
Absorption correction	no correction	no correction	SADABS <sup>[66]</sup>	
Max /min_transmission	0.77/0.66	0 51/0 45	0.60/0.52	
	90(2)	90(2)	90(1)	
$M_{\rm OX} = 2A [^{\rm O}]$	54.12	50.04	50.04	
Nax. 20 [ ]	34.12 25077	524021	50.04	
Reflections measured	23977	324031	090003	
Unique reflections	5683	12379	12/98	
R <sub>int</sub>	0.036	0.0429	0.0637	
Parameters, restraints	425, 0	450, 0	458, 0	
Reflections $[F_{\rm o} > 2\sigma(F_{\rm o})]$	4983	9398	8774	
$R_1 \left[ F_{\rm o} > 2\sigma(F_{\rm o}) \right]$	0.0404	0.0984	0.0935	
$wR_2$ (all data) <sup>[a]</sup>	0.1064	0.2904	0.3181	
a	0.0341	0.1060	0.1330	
b	8.2311	2219.48	2964.08	
G.O.F.	1.082	1.132	1.054	
Restr. G.O.F.	1.082	1.132	1.054	
CCDC number	260289	286142	286143	
	6	7	11	12
	6	7	11	12
Structural formula	$\frac{6}{Zn(Et_2dtc)_2 \cdot C_{60} \cdot (C_6H_5Cl)_{0.5} \cdot (C_6H_6)_{0.5}}$	7 $[Cd(Et_2dtc)_2]_2 \cdot C_{60}$	<b>11</b> [Cu(EtMedtc) <sub>2</sub> ] <sub>2</sub> •C <sub>60</sub>	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$
Structural formula Empirical formula	$\frac{6}{Zn(Et_2dtc)_2 \cdot C_{60} \cdot (C_6H_5Cl)_{0.5} \cdot (C_6H_6)_{0.5}}$ $C_{76}H_{25} \cdot Scl_0 \cdot SN_2S_4Zn$	7 $[Cd(Et_2dtc)_2]_2 \cdot C_{60}$ $C_{80}H_{40}Cd_2N_4S_8$	11 $[Cu(EtMedtc)_2]_2 \cdot C_{60}$ $C_{76}H_{32}Cu_2N_4S_8$	<b>12</b> [Zn(EtMedtc) <sub>2</sub> ] <sub>3</sub> ·(C <sub>60</sub> ) <sub>2</sub> C <sub>144</sub> H <sub>54</sub> N <sub>6</sub> S <sub>12</sub> Zn <sub>3</sub>
Structural formula Empirical formula M <sub>r</sub> [g·mol <sup>-1</sup> ]	$\frac{6}{Zn(Et_2dtc)_2 \cdot C_{60} \cdot (C_6H_5Cl)_{0.5} \cdot (C_6H_6)_{0.5}} \\ C_{76}H_{25.5}Cl_{0.5}N_2S_4Zn \\ 1177.82$	7 $[Cd(Et_2dtc)_2]_2 \cdot C_{60}$ $C_{80}H_{40}Cd_2N_4S_8$ 1538.44	11 $[Cu(EtMedtc)_2]_2 \cdot C_{60}$ $C_{76}H_{32}Cu_2N_4S_8$ 1384.62	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color	<b>6</b> $Zn(Et_2dtc)_2 \cdot C_{60} \cdot (C_6H_5Cl)_{0.5} \cdot (C_6H_6)_{0.5}$ $C_{76}H_{25.5}Cl_{0.5}N_2S_4Zn$ 1177.82 black parallelepipeds	7 $[Cd(Et_2dtc)_2]_2 \cdot C_{60}$ $C_{80}H_{40}Cd_2N_4S_8$ 1538.44 brown rhombus	11 $[Cu(EtMedtc)_2]_2 \cdot C_{60}$ $C_{76}H_{32}Cu_2N_4S_8$ 1384.62 black rhombus	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71 black rhombus
Structural formula Empirical formula M <sub>r</sub> [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm]	$\frac{6}{2n(Et_2dtc)_2 \cdot C_{60} \cdot (C_6H_5Cl)_{0.5} \cdot (C_6H_6)_{0.5}} \\ C_{76}H_{25.5}Cl_{0.5}N_2S_4Zn \\ 1177.82 \\ black parallelepipeds \\ 0.33 \times 0.20 \times 0.20 \\ \end{array}$	7 $[Cd(Et_2dtc)_2]_2 \cdot C_{60}$ $C_{80}H_{40}Cd_2N_4S_8$ 1538.44 brown rhombus $0.40 \times 0.30 \times 0.10$	$\begin{array}{c} \textbf{11} \\ [Cu(EtMedtc)_2]_2 \cdot C_{60} \\ C_{76}H_{32}Cu_2N_4S_8 \\ 1384.62 \\ black rhombus \\ 0.42 \times 0.38 \times 0.10 \end{array}$	$\begin{array}{c} \textbf{12} \\ \hline [Zn(EtMedtc)_2]_3 \cdot (C_{60})_2 \\ C_{144}H_{54}N_6S_{12}Zn_3 \\ 2442.71 \\ black rhombus \\ 0.40 \times 0.30 \times 0.20 \end{array}$
Structural formula Empirical formula M <sub>r</sub> [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system		7 $[Cd(Et_2dtc)_2]_2 \cdot C_{60}$ $C_{80}H_{40}Cd_2N_4S_8$ 1538.44 brown rhombus $0.40 \times 0.30 \times 0.10$ monoclinic	$\begin{array}{c} \textbf{11} \\ [Cu(EtMedtc)_2]_2 \cdot C_{60} \\ C_{76}H_{32}Cu_2N_4S_8 \\ 1384.62 \\ black rhombus \\ 0.42 \times 0.38 \times 0.10 \\ monoclinic \end{array}$	$\begin{array}{c} \textbf{12} \\ \hline [Zn(EtMedtc)_{2]_{3}} \cdot (C_{60})_{2} \\ C_{144}H_{54}N_{6}S_{12}Zn_{3} \\ 2442.71 \\ black rhombus \\ 0.40 \times 0.30 \times 0.20 \\ orthorhombic \end{array}$
Structural formula Empirical formula M <sub>r</sub> [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group		7 $[Cd(Et_2dtc)_2]_2 \cdot C_{60}$ $C_{80}H_{40}Cd_2N_4S_8$ 1538.44 brown rhombus $0.40 \times 0.30 \times 0.10$ monoclinic $P_{2.1/c}$	11 [Cu(EtMedtc) <sub>2</sub> ] <sub>2</sub> ·C <sub>60</sub> $C_{76}H_{32}Cu_2N_4S_8$ 1384.62 black rhombus $0.42 \times 0.38 \times 0.10$ monoclinic P2,	12 $[Zn(EtMedtc)_{2}]_{3} \cdot (C_{60})_{2}$ $C_{144}H_{54}N_{6}S_{12}Zn_{3}$ 2442.71 black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_{1a}$
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å]	6 $Zn(Et_2dtc)_2 C_{60} (C_6H_5Cl)_{0.5} (C_6H_6)_{0.5}$ $C_{76}H_{25.5}Cl_{0.5}N_2S_4Zn$ 1177.82 black parallelepipeds $0.33 \times 0.20 \times 0.20$ triclinic $P\bar{1}$ 10 3762(5)	7 $[Cd(Et_2dtc)_2]_2 \cdot C_{60}$ $C_{80}H_{40}Cd_2N_4S_8$ 1538.44 brown rhombus $0.40 \times 0.30 \times 0.10$ monoclinic $P2_1/c$ 16.1712(13)	11 [Cu(EtMedtc) <sub>2</sub> ] <sub>2</sub> ·C <sub>60</sub> $C_{76}H_{32}Cu_2N_4S_8$ 1384.62 black rhombus $0.42 \times 0.38 \times 0.10$ monoclinic $P_{2_1}$ 16 0626(4)	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71 black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ 20.815(5)
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å]	$\frac{6}{2n(Et_2dtc)_2 \cdot C_{60} \cdot (C_6H_5Cl)_{0.5} \cdot (C_6H_6)_{0.5}} C_{76}H_{25.5}Cl_{0.5}N_2S_4Zn \\ 1177.82 \\ black parallelepipeds \\ 0.33 \times 0.20 \times 0.20 \\ triclinic \\ P\overline{I} \\ 10.3762(5) \\ 15.1717(7) \\ \end{bmatrix}$	7 $[Cd(Et_2dtc)_2]_2 \cdot C_{60}$ $C_{80}H_{40}Cd_2N_4S_8$ 1538.44 brown rhombus $0.40 \times 0.30 \times 0.10$ monoclinic $P2_1/c$ 16.1712(13) 16.9680(12)	11 [Cu(EtMedtc) <sub>2</sub> ] <sub>2</sub> ·C <sub>60</sub> $C_{76}H_{32}Cu_2N_4S_8$ 1384.62 black rhombus $0.42 \times 0.38 \times 0.10$ monoclinic $P2_1$ 16.0626(4) 10.0196(3)	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71 black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ 20.815(5) 26.072(6)
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å]	$\frac{6}{2n(Et_2dtc)_2 \cdot C_{60} \cdot (C_6H_5Cl)_{0.5} \cdot (C_6H_6)_{0.5}} \\ C_{76}H_{25.5}Cl_{0.5}N_2S_4Zn \\ 1177.82 \\ black parallelepipeds \\ 0.33 \times 0.20 \times 0.20 \\ triclinic \\ P\bar{1} \\ 10.3762(5) \\ 15.1717(7) \\ 17.0002(8) \\ \end{array}$	7 $[Cd(Et_2dtc)_2]_2 \cdot C_{60}$ $C_{80}H_{40}Cd_2N_4S_8$ 1538.44 brown rhombus 0.40 × 0.30 × 0.10 monoclinic $P2_1/c$ 16.1712(13) 16.9680(12) 10.525(8)	11 [Cu(EtMedtc) <sub>2</sub> ] <sub>2</sub> ·C <sub>60</sub> $C_{76}H_{32}Cu_2N_4S_8$ 1384.62 black rhombus $0.42 \times 0.38 \times 0.10$ monoclinic $P2_1$ 16.0626(4) 10.0196(3) 17.0653(5)	12 $[Zn(EtMedtc)_2]_3 (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71 black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ 20.815(5) 26.072(6) 17.128(4)
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] b [Å] c [Å]	$\frac{6}{2n(Et_2dtc)_2 \cdot C_{60} \cdot (C_6H_5Cl)_{0.5} \cdot (C_6H_6)_{0.5}} \\ C_{76}H_{25.5}Cl_{0.5}N_2S_4Zn \\ 1177.82 \\ black parallelepipeds \\ 0.33 \times 0.20 \times 0.20 \\ triclinic \\ P\overline{1} \\ 10.3762(5) \\ 15.1717(7) \\ 17.0002(8) \\ 115 892(1) \\ \end{array}$	7 $[Cd(Et_2dtc)_2]_2 \cdot C_{60}$ $C_{80}H_{40}Cd_2N_4S_8$ 1538.44 brown rhombus 0.40 × 0.30 × 0.10 monoclinic $P2_1/c$ 16.1712(13) 16.9680(12) 10.5355(8) 90	11 [Cu(EtMedtc) <sub>2</sub> ] <sub>2</sub> ·C <sub>60</sub> $C_{76}H_{32}Cu_2N_4S_8$ 1384.62 black rhombus $0.42 \times 0.38 \times 0.10$ monoclinic $P2_1$ 16.0626(4) 10.0196(3) 17.0653(5) 90	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71 black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ 20.815(5) 26.072(6) 17.128(4) 90
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] b [Å] c [Å] c [Å] a [°]		7 $[Cd(Et_2dtc)_2]_2 \cdot C_{60}$ $C_{80}H_{40}Cd_2N_4S_8$ 1538.44 brown rhombus $0.40 \times 0.30 \times 0.10$ monoclinic $P2_1/c$ 16.1712(13) 16.9680(12) 10.5355(8) 90 90 90 90 90 90 90 90 90 90	11 [Cu(EtMedtc) <sub>2</sub> ] <sub>2</sub> ·C <sub>60</sub> $C_{76}H_{32}Cu_2N_4S_8$ 1384.62 black rhombus $0.42 \times 0.38 \times 0.10$ monoclinic $P2_1$ 16.0626(4) 10.0196(3) 17.0653(5) 90 100.0400(12)	12 [Zn(EtMedtc) <sub>2</sub> ] <sub>3</sub> ·(C <sub>60</sub> ) <sub>2</sub> $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71 black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic <i>Pn</i> 2 <sub>1</sub> <i>a</i> 20.815(5) 26.072(6) 17.128(4) 90
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] c [Å] a [°] $\beta$ [°]		7 $[Cd(Et_2dtc)_2]_2 \cdot C_{60}$ $C_{80}H_{40}Cd_2N_4S_8$ 1538.44 brown rhombus $0.40 \times 0.30 \times 0.10$ monoclinic $P2_1/c$ 16.1712(13) 16.9680(12) 10.5355(8) 90 99.857(2)	11 [Cu(EtMedtc) <sub>2</sub> ] <sub>2</sub> ·C <sub>60</sub> $C_{76}H_{32}Cu_2N_4S_8$ 1384.62 black rhombus $0.42 \times 0.38 \times 0.10$ monoclinic $P2_1$ 16.0626(4) 10.0196(3) 17.0653(5) 90 100.9490(13) $\infty$	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71 black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ 20.815(5) 26.072(6) 17.128(4) 90 90 90
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] b [Å] c [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°]		7 $[Cd(Et_2dtc)_2]_2 \cdot C_{60}$ $C_{80}H_{40}Cd_2N_4S_8$ 1538.44 brown rhombus $0.40 \times 0.30 \times 0.10$ monoclinic $P2_1/c$ 16.1712(13) 16.9680(12) 10.3355(8) 90 99.857(2) 90	11 [Cu(EtMedtc) <sub>2</sub> ] <sub>2</sub> ·C <sub>60</sub> $C_{76}H_{32}Cu_2N_4S_8$ 1384.62 black rhombus $0.42 \times 0.38 \times 0.10$ monoclinic $P2_1$ 16.0626(4) 10.0196(3) 17.0653(5) 90 100.9490(13) 90 90 90 90 90 90 90 90 90 90	12 $[Zn(EtMedtc)_{2}]_{3} \cdot (C_{60})_{2}$ $C_{144}H_{54}N_{6}S_{12}Zn_{3}$ 2442.71 black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_{1}a$ 20.815(5) 26.072(6) 17.128(4) 90 90 90 90 90 90
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] a [Å] a [°] $\beta$ [°] $\gamma$ [°] $\gamma$ [°] V [Å <sup>3</sup> ]		7 $\begin{bmatrix} Cd(Et_2dtc)_2 \end{bmatrix}_2 \cdot C_{60} \\ C_{80}H_{40}Cd_2N_4S_8 \\ 1538.44 \\ brown rhombus \\ 0.40 \times 0.30 \times 0.10 \\ monoclinic \\ P2_1/c \\ 16.1712(13) \\ 16.9680(12) \\ 10.5355(8) \\ 90 \\ 99.857(2) \\ 90 \\ 2848.2(4) \\ 2848.$	$\begin{array}{c} \textbf{11} \\ \hline \\ [Cu(EtMedtc)_2]_2 \cdot C_{60} \\ C_{76}H_{32}Cu_2N_4S_8 \\ 1384.62 \\ black rhombus \\ 0.42 \times 0.38 \times 0.10 \\ monoclinic \\ P2_1 \\ 16.0626(4) \\ 10.0196(3) \\ 17.0653(5) \\ 90 \\ 100.9490(13) \\ 90 \\ 2696.51(13) \end{array}$	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71 black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ 20.815(5) 26.072(6) 17.128(4) 90 90 90 9298.88(12)
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z		7 $\begin{bmatrix} Cd(Et_2dtc)_2]_2 \cdot C_{60} \\ C_{80}H_{40}Cd_2N_4S_8 \\ 1538.44 \\ brown rhombus \\ 0.40 \times 0.30 \times 0.10 \\ monoclinic \\ P2_1/c \\ 16.1712(13) \\ 16.9680(12) \\ 10.5355(8) \\ 90 \\ 99.857(2) \\ 90 \\ 2848.2(4) \\ 2 \\ 1.701 $	11 [Cu(EtMedtc) <sub>2</sub> ] <sub>2</sub> ·C <sub>60</sub> $C_{76}H_{32}Cu_2N_4S_8$ 1384.62 black rhombus $0.42 \times 0.38 \times 0.10$ monoclinic $P2_1$ 16.0626(4) 10.0196(3) 17.0653(5) 90 100.9490(13) 90 2696.51(13) 2	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71 black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ 20.815(5) 26.072(6) 17.128(4) 90 90 90 9298.88(12) 4
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{calc}$ [g/cm <sup>3</sup> ]		7 $\begin{bmatrix} Cd(Et_2dtc)_2]_2 \cdot C_{60} \\ C_{80}H_{40}Cd_2N_4S_8 \\ 1538.44 \\ brown rhombus \\ 0.40 \times 0.30 \times 0.10 \\ monoclinic \\ P2_1/c \\ 16.1712(13) \\ 16.9680(12) \\ 10.5355(8) \\ 90 \\ 99.857(2) \\ 90 \\ 2848.2(4) \\ 2 \\ 1.794 \\ 0 \end{bmatrix}$	$\begin{array}{c} \textbf{11} \\ \hline \textbf{[Cu(EtMedtc)_2]_2\cdot C_{60}} \\ C_{76}H_{32}Cu_2N_4S_8 \\ 1384.62 \\ black rhombus \\ 0.42 \times 0.38 \times 0.10 \\ monoclinic \\ P2_1 \\ 16.0626(4) \\ 10.0196(3) \\ 17.0653(5) \\ 90 \\ 100.9490(13) \\ 90 \\ 2696.51(13) \\ 2 \\ 1.705 \\ \end{array}$	$\begin{array}{c} \textbf{12} \\ \hline [Zn(EtMedtc)_2]_3 \cdot (C_{60})_2 \\ C_{144}H_{54}N_6S_{12}Zn_3 \\ 2442.71 \\ black rhombus \\ 0.40 \times 0.30 \times 0.20 \\ orthorhombic \\ Pn2_1a \\ 20.815(5) \\ 26.072(6) \\ 17.128(4) \\ 90 \\ 90 \\ 90 \\ 9298.88(12) \\ 4 \\ 1.746 \end{array}$
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] b [Å] c [Å] a [°] $\gamma$ [°] $\gamma$ [°] $\gamma$ [°] $\gamma$ [ $\zeta$ ] Z $\rho_{calc}$ [g/cm <sup>3</sup> ] $\mu$ [mm <sup>-1</sup> ]		$\begin{array}{c} 7\\ \hline \\ [Cd(Et_2dtc)_2]_2 \cdot C_{60} \\ C_{80}H_{40}Cd_2N_4S_8 \\ 1538.44 \\ brown rhombus \\ 0.40 \times 0.30 \times 0.10 \\ monoclinic \\ P2_1/c \\ 16.1712(13) \\ 16.9680(12) \\ 10.5355(8) \\ 90 \\ 99.857(2) \\ 90 \\ 2848.2(4) \\ 2 \\ 1.794 \\ 1.098 \end{array}$	$\begin{array}{c} \textbf{11} \\ [Cu(EtMedtc)_2]_2 \cdot C_{60} \\ C_{76}H_{32}Cu_2N_4S_8 \\ 1384.62 \\ black rhombus \\ 0.42 \times 0.38 \times 0.10 \\ monoclinic \\ P2_1 \\ 16.0626(4) \\ 10.0196(3) \\ 17.0653(5) \\ 90 \\ 100.9490(13) \\ 90 \\ 2696.51(13) \\ 2 \\ 1.705 \\ 1.156 \end{array}$	$\begin{array}{c} \textbf{12} \\ \hline [Zn(EtMedtc)_2]_3 \cdot (C_{60})_2 \\ C_{144}H_{54}N_6S_{12}Zn_3 \\ 2442.71 \\ black rhombus \\ 0.40 \times 0.30 \times 0.20 \\ orthorhombic \\ Pn2_1a \\ 20.815(5) \\ 26.072(6) \\ 17.128(4) \\ 90 \\ 90 \\ 90 \\ 90 \\ 9298.88(12) \\ 4 \\ 1.746 \\ 1.109 \\ \end{array}$
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] b [Å] c [Å] c [Å] g [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{calc}$ [g/cm <sup>3</sup> ] $\mu$ [mm <sup>-1</sup> ] F(000)		$\begin{array}{c} 7\\ \hline \\ [Cd(Et_2dtc)_2]_2 \cdot C_{60} \\ C_{80}H_{40}Cd_2N_4S_8 \\ 1538.44 \\ brown rhombus \\ 0.40 \times 0.30 \times 0.10 \\ monoclinic \\ P2_1/c \\ 16.1712(13) \\ 16.9680(12) \\ 10.5355(8) \\ 90 \\ 99.857(2) \\ 90 \\ 2848.2(4) \\ 2 \\ 1.794 \\ 1.098 \\ 1544 \\ \end{array}$	$\begin{array}{c} \textbf{11} \\ [Cu(EtMedtc)_2]_2 \cdot C_{60} \\ C_{76}H_{32}Cu_2N_4S_8 \\ 1384.62 \\ black rhombus \\ 0.42 \times 0.38 \times 0.10 \\ monoclinic \\ P2_1 \\ 16.0626(4) \\ 10.0196(3) \\ 17.0653(5) \\ 90 \\ 100.9490(13) \\ 90 \\ 2696.51(13) \\ 2 \\ 1.705 \\ 1.156 \\ 1404 \end{array}$	$\begin{array}{c} \textbf{12} \\ \hline [Zn(EtMedtc)_{2]_{3}} \cdot (C_{60})_{2} \\ C_{144}H_{54}N_{6}S_{12}Zn_{3} \\ 2442.71 \\ black rhombus \\ 0.40 \times 0.30 \times 0.20 \\ orthorhombic \\ Pn2_{1}a \\ 20.815(5) \\ 26.072(6) \\ 17.128(4) \\ 90 \\ 90 \\ 90 \\ 90 \\ 9298.88(12) \\ 4 \\ 1.746 \\ 1.109 \\ 4944 \\ \end{array}$
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å] Z $\rho_{calc}$ [g/cm <sup>3</sup> ] $\mu$ [mm <sup>-1</sup> ] F(000)		$\begin{array}{c} 7\\ \hline \\ [Cd(Et_2dtc)_2]_2 \cdot C_{60}\\ C_{80}H_{40}Cd_2N_4S_8\\ 1538.44\\ brown rhombus\\ 0.40 \times 0.30 \times 0.10\\ monoclinic\\ P2_1/c\\ 16.1712(13)\\ 16.9680(12)\\ 10.5355(8)\\ 90\\ 99.857(2)\\ 90\\ 2848.2(4)\\ 2\\ 1.794\\ 1.098\\ 1544\\ SADABS^{[66]}\\ \end{array}$	$\begin{array}{c} \textbf{11} \\ \hline \\ [Cu(EtMedtc)_2]_2 \cdot C_{60} \\ C_{76}H_{32}Cu_2N_4S_8 \\ 1384.62 \\ black rhombus \\ 0.42 \times 0.38 \times 0.10 \\ monoclinic \\ P2_1 \\ 16.0626(4) \\ 10.0196(3) \\ 17.0653(5) \\ 90 \\ 100.9490(13) \\ 90 \\ 2696.51(13) \\ 2 \\ 1.705 \\ 1.156 \\ 1404 \\ no correction \\ \end{array}$	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71 black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ 20.815(5) 26.072(6) 17.128(4) 90 90 90 9298.88(12) 4 1.746 1.109 4944 no correction
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{calc}$ [g/cm <sup>3</sup> ] $\mu$ [mm <sup>-1</sup> ] F(000) Absorption correction Max./min. transmission		$\begin{array}{c} 7\\ \hline \\ [Cd(Et_2dtc)_2]_2 \cdot C_{60} \\ C_{80}H_{40}Cd_2N_4S_8 \\ 1538.44 \\ brown rhombus \\ 0.40 \times 0.30 \times 0.10 \\ monoclinic \\ P2_1/c \\ 16.1712(13) \\ 16.9680(12) \\ 10.5355(8) \\ 90 \\ 99.857(2) \\ 90 \\ 2848.2(4) \\ 2 \\ 1.794 \\ 1.098 \\ 1544 \\ SADABS^{[66]} \\ 0.90/0.72 \\ \end{array}$	$\begin{array}{c} \textbf{11} \\ \hline \\ [Cu(EtMedtc)_2]_2 \cdot C_{60} \\ C_{76}H_{32}Cu_2N_4S_8 \\ 1384.62 \\ black rhombus \\ 0.42 \times 0.38 \times 0.10 \\ monoclinic \\ P2_1 \\ 16.0626(4) \\ 10.0196(3) \\ 17.0653(5) \\ 90 \\ 100.9490(13) \\ 90 \\ 2696.51(13) \\ 2 \\ 1.705 \\ 1.156 \\ 1404 \\ no correction \\ 0.89/0.64 \\ \end{array}$	$\begin{array}{c} \textbf{12} \\ \hline [Zn(EtMedtc)_2]_3 \cdot (C_{60})_2 \\ C_{144}H_{54}N_6S_{12}Zn_3 \\ 2442.71 \\ black rhombus \\ 0.40 \times 0.30 \times 0.20 \\ orthorhombic \\ Pn2_1a \\ 20.815(5) \\ 26.072(6) \\ 17.128(4) \\ 90 \\ 90 \\ 90 \\ 90 \\ 9298.88(12) \\ 4 \\ 1.746 \\ 1.109 \\ 4944 \\ no correction \\ 0.81/0.66 \\ \end{array}$
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{calc}$ [g/cm <sup>3</sup> ] $\mu$ [mm <sup>-1</sup> ] F(000) Absorption correction Max./min. transmission T [K]		$\begin{array}{c} 7\\ \hline \\ [Cd(Et_2dtc)_2]_2 \cdot C_{60}\\ C_{80}H_{40}Cd_2N_4S_8\\ 1538.44\\ brown rhombus\\ 0.40 \times 0.30 \times 0.10\\ monoclinic\\ P2_1/c\\ 16.1712(13)\\ 16.9680(12)\\ 10.5355(8)\\ 90\\ 99.857(2)\\ 90\\ 99.857(2)\\ 90\\ 2848.2(4)\\ 2\\ 1.794\\ 1.098\\ 1544\\ SADABS^{[66]}\\ 0.90/0.72\\ 123(2)\\ \end{array}$	$\begin{array}{c} \textbf{11} \\ \hline \\ [Cu(EtMedtc)_2]_2 \cdot C_{60} \\ C_{76}H_{32}Cu_2N_4S_8 \\ 1384.62 \\ black rhombus \\ 0.42 \times 0.38 \times 0.10 \\ monoclinic \\ P2_1 \\ 16.0626(4) \\ 10.0196(3) \\ 17.0653(5) \\ 90 \\ 100.9490(13) \\ 90 \\ 2696.51(13) \\ 2 \\ 1.705 \\ 1.156 \\ 1404 \\ no correction \\ 0.89/0.64 \\ 100(2) \end{array}$	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71 black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ 20.815(5) 26.072(6) 17.128(4) 90 90 90 9298.88(12) 4 1.746 1.109 4944 no correction 0.81/0.66 100(2)
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [6] $\gamma$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{calc}$ [g/cm <sup>3</sup> ] $\mu$ [mm <sup>-1</sup> ] F(000) Absorption correction Max./min. transmission T [K] Max. 2 $\theta$ [°]		$\begin{array}{c} 7\\ \hline \\ [Cd(Et_2dtc)_2]_2 \cdot C_{60} \\ C_{80}H_{40}Cd_2N_4S_8 \\ 1538.44 \\ brown rhombus \\ 0.40 \times 0.30 \times 0.10 \\ monoclinic \\ P2_1/c \\ 16.1712(13) \\ 16.9680(12) \\ 10.5355(8) \\ 90 \\ 99.857(2) \\ 90 \\ 2848.2(4) \\ 2 \\ 1.794 \\ 1.098 \\ 1544 \\ SADABS^{[66]} \\ 0.90/0.72 \\ 123(2) \\ 51.88 \\ \end{array}$	$\begin{array}{c} \textbf{11} \\ \hline \\ [Cu(EtMedtc)_2]_2 \cdot C_{60} \\ C_{76}H_{32}Cu_2N_4S_8 \\ 1384.62 \\ black rhombus \\ 0.42 \times 0.38 \times 0.10 \\ monoclinic \\ P2_1 \\ 16.0626(4) \\ 10.0196(3) \\ 17.0653(5) \\ 90 \\ 100.9490(13) \\ 90 \\ 2696.51(13) \\ 2 \\ 1.705 \\ 1.156 \\ 1404 \\ no correction \\ 0.89/0.64 \\ 100(2) \\ 54.96 \end{array}$	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71 black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ 20.815(5) 26.072(6) 17.128(4) 90 90 90 9298.88(12) 4 1.746 1.109 4944 no correction 0.81/0.66 100(2) 51.48
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{calc}$ [g/cm <sup>3</sup> ] $\mu$ [mm <sup>-1</sup> ] F(000) Absorption correction Max./min. transmission T [K] Max. $2\theta$ [°] Reflections measured		$\begin{array}{c} 7\\ \hline \\ [Cd(Et_2dtc)_2]_2 \cdot C_{60} \\ C_{80}H_{40}Cd_2N_4S_8 \\ 1538.44 \\ brown rhombus \\ 0.40 \times 0.30 \times 0.10 \\ monoclinic \\ P2_1/c \\ 16.1712(13) \\ 16.9680(12) \\ 10.5355(8) \\ 90 \\ 99.857(2) \\ 90 \\ 2848.2(4) \\ 2 \\ 1.794 \\ 1.098 \\ 1544 \\ SADABS^{[66]} \\ 0.90/0.72 \\ 123(2) \\ 51.88 \\ 13023 \\ \end{array}$	$\begin{array}{c} \textbf{11} \\ \hline \\ [Cu(EtMedtc)_2]_2 \cdot C_{60} \\ C_{76}H_{32}Cu_2N_4S_8 \\ 1384.62 \\ black rhombus \\ 0.42 \times 0.38 \times 0.10 \\ monoclinic \\ P2_1 \\ 16.0626(4) \\ 10.0196(3) \\ 17.0653(5) \\ 90 \\ 100.9490(13) \\ 90 \\ 2696.51(13) \\ 2 \\ 1.705 \\ 1.156 \\ 1404 \\ no correction \\ 0.89/0.64 \\ 100(2) \\ 54.96 \\ 20222 \\ \end{array}$	12 [Zn(EtMedtc) <sub>2</sub> ] <sub>3</sub> ·(C <sub>60</sub> ) <sub>2</sub> $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71 black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic <i>Pn2</i> <sub>1</sub> <i>a</i> 20.815(5) 26.072(6) 17.128(4) 90 90 9298.88(12) 4 1.746 1.109 4944 no correction 0.81/0.66 100(2) 51.48 42780
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$		$\begin{array}{c} 7\\ \hline \\ \hline [Cd(Et_2dtc)_2]_2 \cdot C_{60} \\ \hline \\ C_{80}H_{40}Cd_2N_4S_8 \\ 1538.44 \\ \hline \\ brown rhombus \\ 0.40 \times 0.30 \times 0.10 \\ monoclinic \\ P2_1/c \\ 16.1712(13) \\ 16.9680(12) \\ 10.5355(8) \\ 90 \\ 99.857(2) \\ 90 \\ 99.857(2) \\ 90 \\ 2848.2(4) \\ 2 \\ 1.794 \\ 1.098 \\ 1544 \\ SADABS^{[66]} \\ 0.90/0.72 \\ 123(2) \\ 51.88 \\ 13023 \\ 3602 \\ \end{array}$	$\begin{array}{c} \textbf{11} \\ \hline \\ [Cu(EtMedtc)_2]_2 \cdot C_{60} \\ C_{76}H_{32}Cu_2N_4S_8 \\ 1384.62 \\ black rhombus \\ 0.42 \times 0.38 \times 0.10 \\ monoclinic \\ P2_1 \\ 16.0626(4) \\ 10.0196(3) \\ 17.0653(5) \\ 90 \\ 100.9490(13) \\ 90 \\ 2696.51(13) \\ 2 \\ 1.705 \\ 1.156 \\ 1404 \\ no correction \\ 0.89/0.64 \\ 100(2) \\ 54.96 \\ 20222 \\ 11660 \\ \end{array}$	12 [Zn(EtMedtc) <sub>2</sub> ] <sub>3</sub> ·( $C_{60}$ ) <sub>2</sub> $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71 black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ 20.815(5) 26.072(6) 17.128(4) 90 90 90 90 9298.88(12) 4 1.746 1.109 4944 no correction 0.81/0.66 100(2) 51.48 42780 17592
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{calc}$ [g/cm <sup>3</sup> ] $\mu$ [mm <sup>-1</sup> ] F(000) Absorption correction Max./min. transmission T [K] Max. 2 $\theta$ [°] Reflections measured Unique reflections $R_{int}$		$\begin{array}{c} 7\\ \hline \\ [Cd(Et_2dtc)_2]_2 \cdot C_{60} \\ C_{80}H_{40}Cd_2N_4S_8 \\ 1538.44 \\ brown rhombus \\ 0.40 \times 0.30 \times 0.10 \\ monoclinic \\ P_{2_1/c} \\ 16.1712(13) \\ 16.9680(12) \\ 10.5355(8) \\ 90 \\ 99.857(2) \\ 90 \\ 2848.2(4) \\ 2 \\ 1.794 \\ 1.098 \\ 1544 \\ SADABS^{[66]} \\ 0.90/0.72 \\ 123(2) \\ 51.88 \\ 13023 \\ 3602 \\ 0.0333 \\ \end{array}$	$\begin{array}{c} \textbf{11} \\ \hline \\ [Cu(EtMedtc)_2]_2 \cdot C_{60} \\ C_{76}H_{32}Cu_2N_4S_8 \\ 1384.62 \\ black rhombus \\ 0.42 \times 0.38 \times 0.10 \\ monoclinic \\ P2_1 \\ 16.0626(4) \\ 10.0196(3) \\ 17.0653(5) \\ 90 \\ 100.9490(13) \\ 90 \\ 2696.51(13) \\ 2 \\ 1.705 \\ 1.156 \\ 1404 \\ no \ correction \\ 0.89/0.64 \\ 100(2) \\ 54.96 \\ 20222 \\ 11660 \\ \end{array}$	12 [Zn(EtMedtc) <sub>2</sub> ] <sub>3</sub> ·( $C_{60}$ ) <sub>2</sub> $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71 black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ 20.815(5) 26.072(6) 17.128(4) 90 90 90 9298.88(12) 4 1.746 1.109 4944 no correction 0.81/0.66 100(2) 51.48 42780 17592
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°]		$\begin{array}{c} 7\\ \hline \\ $	11 [Cu(EtMedtc) <sub>2</sub> ] <sub>2</sub> ·C <sub>60</sub> $C_{76}H_{32}Cu_2N_4S_8$ 1384.62 black rhombus $0.42 \times 0.38 \times 0.10$ monoclinic $P2_1$ 16.0626(4) 10.0196(3) 17.0653(5) 90 100.9490(13) 90 2696.51(13) 2 1.705 1.156 1404 no correction 0.89/0.64 100(2) 54.96 20222 11660 812, 0	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ $2442.71$ black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ $20.815(5)$ $26.072(6)$ $17.128(4)$ 90         90         90         90         9298.88(12)         4 $1.746$ $1.109$ 4944         no correction $0.81/0.66$ $100(2)$ $51.48$ $42780$ $17592$ $2393, 11252$
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{calc}$ [g/cm <sup>3</sup> ] $\mu$ [mm <sup>-1</sup> ] F(000) Absorption correction Max./min. transmission T [K] Max. $2\theta$ [°] Reflections measured Unique reflections $R_{int}$ Parameters, restraints Reflections [ $F_c > 2\pi(F_c)$ ]		$\begin{array}{c} 7\\ \hline \\ \hline [Cd(Et_2dtc)_2]_2 \cdot C_{60} \\ C_{80}H_{40}Cd_2N_4S_8 \\ 1538.44 \\ brown rhombus \\ 0.40 \times 0.30 \times 0.10 \\ monoclinic \\ P2_1/c \\ 16.1712(13) \\ 16.9680(12) \\ 10.5355(8) \\ 90 \\ 99 \\ 99.857(2) \\ 90 \\ 2848.2(4) \\ 2 \\ 1.794 \\ 1.098 \\ 1544 \\ SADABS^{[66]} \\ 0.90/0.72 \\ 123(2) \\ 51.88 \\ 13023 \\ 3602 \\ 0.0333 \\ 424, 423 \\ 3100 \\ \end{array}$	11 [Cu(EtMedtc) <sub>2</sub> ] <sub>2</sub> ·C <sub>60</sub> $C_{76}H_{32}Cu_2N_4S_8$ 1384.62 black rhombus $0.42 \times 0.38 \times 0.10$ monoclinic $P2_1$ 16.0626(4) 10.0196(3) 17.0653(5) 90 100.9490(13) 90 2696.51(13) 2 1.705 1.156 1404 no correction 0.89/0.64 100(2) 54.96 20222 11660 812, 0 10282	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ $2442.71$ black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ $20.815(5)$ $26.072(6)$ $17.128(4)$ $90$ $90$ $9298.88(12)$ $4$ $1.746$ $1.109$ $4944$ no correction $0.81/0.66$ $100(2)$ $51.48$ $42780$ $17592$ $2393, 11252$
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{calc}$ [g/cm <sup>3</sup> ] $\mu$ [mm <sup>-1</sup> ] F(000) Absorption correction Max./min. transmission T [K] Max. $2\theta$ [°] Reflections measured Unique reflections $R_{int}$ Parameters, restraints Reflections [ $F_o > 2\sigma(F_o)$ ] $R_i$ [ $F_i > 2\sigma(F_i)$ ]		$\begin{array}{c} 7\\ \hline \\ $	11 [Cu(EtMedtc) <sub>2</sub> ] <sub>2</sub> ·C <sub>60</sub> $C_{76}H_{32}Cu_2N_4S_8$ 1384.62 black rhombus $0.42 \times 0.38 \times 0.10$ monoclinic $P2_1$ 16.0626(4) 10.0196(3) 17.0653(5) 90 2696.51(13) 2 1.705 1.156 1404 no correction 0.89/0.64 100(2) 54.96 20222 11660 812, 0 10282 0.0381	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ $2442.71$ black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ $20.815(5)$ $26.072(6)$ $17.128(4)$ $90$ $90$ $90$ $9298.88(12)$ $4$ $1.746$ $1.109$ $4944$ no correction $0.81/0.66$ $100(2)$ $51.48$ $42780$ $17592$ $2393, 11252$ $8450$ $0.1038$
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [6] $\gamma$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{calc}$ [g/cm <sup>3</sup> ] $\mu$ [mm <sup>-1</sup> ] F(000) Absorption correction Max./min. transmission T [K] Max. $2\theta$ [°] Reflections measured Unique reflections $R_{int}$ Parameters, restraints Reflections [ $F_o > 2\sigma(F_o)$ ] $R_1$ [ $F_o > 2\sigma(F_o)$ ] $R_1$ [ $d_1 d_21$ ] <sup>[a]</sup>		$\begin{array}{c} 7\\ \hline \\ $	11 [Cu(EtMedtc) <sub>2</sub> ] <sub>2</sub> ·C <sub>60</sub> $C_{76}H_{32}Cu_2N_4S_8$ 1384.62 black rhombus $0.42 \times 0.38 \times 0.10$ monoclinic $P2_1$ 16.0626(4) 10.0196(3) 17.0653(5) 90 2696.51(13) 2 1.705 1.156 1404 no correction 0.89/0.64 100(2) 54.96 20222 11660 812, 0 10282 0.0381 0 0902	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ 2442.71         black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ 20.815(5)         26.072(6)         17.128(4)         90         90         90         9298.88(12)         4         1.746         1.109         4944         no correction         0.81/0.66         100(2)         51.48         42780         17592         2393, 11252         8450         0.1038         0 3023
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å] Z $\rho_{calc}$ [g/cm <sup>3</sup> ] $\mu$ [mm <sup>-1</sup> ] F(000) Absorption correction Max./min. transmission T [K] Max. $2\theta$ [°] Reflections measured Unique reflections $R_{int}$ Parameters, restraints Reflections [ $F_o > 2\sigma(F_o)$ ] $R_1$ [ $F_o > 2\sigma(F_o)$ ] $R_1$ [ $F_o > 2\sigma(F_o)$ ] $R_1$ [ $F_0 > 2\sigma(F_o)$ ] $R_1$ [ $F_0 > 2\sigma(F_o)$ ]		$\begin{array}{c} 7\\ \hline \\ $	11 $[Cu(EtMedic)_2]_2 \cdot C_{60}$ $C_{76}H_{32}Cu_2N_4S_8$ 1384.62           black rhombus $0.42 \times 0.38 \times 0.10$ monoclinic $P2_1$ 16.0626(4)           10.0196(3)           17.0653(5)           90           100.9490(13)           90           2696.51(13)           2           1.705           1.156           1404           no correction           0.89/0.64           100(2)           54.96           20222           11660           812, 0           10282           0.0381           0.0902	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ $2442.71$ black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ $20.815(5)$ $26.072(6)$ $17.128(4)$ $90$ $90$ $90$ $9298.88(12)$ $4$ $1.746$ $1.109$ $4944$ no correction $0.81/0.66$ $100(2)$ $51.48$ $42780$ $17592$ $2393, 11252$ $8450$ $0.1038$ $0.3023$ $0.1956$
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] $\gamma$ [°] $\gamma$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{calc}$ [g/cm <sup>3</sup> ] $\mu$ [mm <sup>-1</sup> ] F(000) Absorption correction Max./min. transmission T [K] Max. 2 $\theta$ [°] Reflections measured Unique reflections $R_{int}$ Parameters, restraints Reflections [ $F_o > 2\sigma(F_o)$ ] $wR_2$ (all data) <sup>[a]</sup> a b		$\begin{array}{c} 7\\ \hline \\ $	$\begin{array}{c} \textbf{11} \\ \hline \\ \hline \\ \begin{bmatrix} \text{Cu}(\text{EtMedtc})_2]_2\cdot\text{C}_{60} \\ \text{C}_{76}\text{H}_{32}\text{Cu}_2\text{N}_4\text{S}_8 \\ 1384.62 \\ 1384.62 \\ 1384.62 \\ 1384.64 \\ 1384.62 \\ 1384.62 \\ 1384.62 \\ 1384.62 \\ 1384.62 \\ 1384.62 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100.98 \\ 0.0196(3) \\ 17.0653(5) \\ 90 \\ 100.9490(13) \\ 90 \\ 2696.51(13) \\ 2 \\ 1.705 \\ 1.156 \\ 1404 \\ 100 \\ 2 \\ 1.705 \\ 1.156 \\ 1404 \\ 100(2) \\ 54.96 \\ 20222 \\ 11660 \\ 812, 0 \\ 10282 \\ 0.0381 \\ 0.0902 \\ 0.0294 \\ 3.4011 \\ 100 \\ 1$	12 $[Zn(EtMedtc)_2]_3$ , $(C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ $2442.71$ black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ $20.815(5)$ $26.072(6)$ $17.128(4)$ $90$ $910$ $90$ $90$ $90$ $90$ $90$ $910$ $9298.88(12)$
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{calc}$ [g/cm <sup>3</sup> ] $\mu$ [mm <sup>-1</sup> ] F(000) Absorption correction Max./min. transmission T [K] Max. $2\theta$ [°] Reflections measured Unique reflections $R_{int}$ Parameters, restraints Reflections [ $F_o > 2\sigma(F_o)$ ] $R_1$ [ $F_o > 2\sigma(F_o)$ ] $wR_2$ (all data) <sup>[a]</sup> a b $G \cap F$		$\begin{array}{c} 7\\ \hline \\ $	$\begin{array}{c} \textbf{11} \\ \hline \\ \hline \\ \begin{bmatrix} \text{Cu(EtMedtc)}_2 \end{bmatrix}_2 \cdot \text{C}_{60} \\ \text{C}_{76}\text{H}_{32}\text{Cu}_2\text{N}_4\text{S}_8 \\ 1384.62 \\ \text{black rhombus} \\ 0.42 \times 0.38 \times 0.10 \\ \text{monoclinic} \\ \hline P2_1 \\ 16.0626(4) \\ 10.0196(3) \\ 17.0653(5) \\ 90 \\ 100.9490(13) \\ 90 \\ 2696.51(13) \\ 2 \\ 1.705 \\ 1.156 \\ 1404 \\ \text{no correction} \\ 0.89/0.64 \\ 100(2) \\ 54.96 \\ 20222 \\ 11660 \\ \hline \\ \textbf{812, 0} \\ 10282 \\ 0.0381 \\ 0.0902 \\ 0.0294 \\ 3.4011 \\ 1 \\ 1023 \\ \hline \end{array}$	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ $2442.71$ black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ $20.815(5)$ $26.072(6)$ $17.128(4)$ 90         90         90         9298.88(12)         4 $1.746$ $1.109$ 4944         no correction $0.81/0.66$ $100(2)$ $51.48$ $42780$ $17592$ $2393, 11252$ $8450$ $0.1038$ $0.3023$ $0.1956$ $0.0000$
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å3] Z $\rho_{calc}$ [g/cm <sup>3</sup> ] $\mu$ [mm <sup>-1</sup> ] F(000) Absorption correction Max./min. transmission T [K] Max. $2\theta$ [°] Reflections measured Unique reflections $R_{int}$ Parameters, restraints Reflections [ $F_0 > 2\sigma(F_0)$ ] $R_1$ [ $F_0 > 2\sigma(F_0)$ ] $wR_2$ (all data) <sup>[a]</sup> a b G.O.F. Beetr. $C.O.F.$		$\begin{array}{c} 7\\ \hline \\ $	11           [Cu(EtMedtc) <sub>2</sub> ] <sub>2</sub> ·C <sub>60</sub> $C_{76}H_{32}Cu_2N_4S_8$ 1384.62           black rhombus           0.42 × 0.38 × 0.10           monoclinic $P2_1$ 16.0626(4)           10.0196(3)           17.0653(5)           90           2696.51(13)           2           1.705           1.156           1404           no correction           0.89/0.64           100(2)           54.96           20222           11660           812, 0           10282           0.0381           0.0902           0.0294           3.4011           1.033	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ $2442.71$ black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ $20.815(5)$ $26.072(6)$ $17.128(4)$ $90$ $90$ $90$ $9298.88(12)$ $4$ $1.746$ $1.109$ $4944$ no correction $0.81/0.66$ $100(2)$ $51.48$ $42780$ $17592$ $2393, 11252$ $8450$ $0.1038$ $0.3023$ $0.1956$ $0.0000$ $0.954$
Structural formula Empirical formula $M_r$ [g·mol <sup>-1</sup> ] Crystal shape and color Size [mm×mm×mm] Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta$ [°] $\gamma$ [°] V [Å <sup>3</sup> ] Z $\rho_{calc}$ [g/cm <sup>3</sup> ] $\mu$ [mm <sup>-1</sup> ] F(000) Absorption correction Max./min. transmission T [K] Max. $2\theta$ [°] Reflections measured Unique reflections $R_{int}$ Parameters, restraints Reflections [ $F_o > 2\sigma(F_o)$ ] $R_1$ [ $F_0 > 2\sigma(F_O$		$\begin{array}{c} 7\\ \hline \\ $	11 $[Cu(EtMedtc)_2]_2 \cdot C_{60}$ $C_{76}H_{32}Cu_2N_4S_8$ 1384.62           black rhombus $0.42 \times 0.38 \times 0.10$ monoclinic $P2_1$ $16.0626(4)$ $10.0196(3)$ $17.0653(5)$ $90$ $2696.51(13)$ $2$ $1.705$ $1.156$ $1404$ no correction $0.89/0.64$ $100(2)$ $54.96$ $20222$ $11660$ $812, 0$ $0.0381$ $0.0294$ $3.4011$ $1.033$ $20222$	12 $[Zn(EtMedtc)_2]_3 \cdot (C_{60})_2$ $C_{144}H_{54}N_6S_{12}Zn_3$ $2442.71$ black rhombus $0.40 \times 0.30 \times 0.20$ orthorhombic $Pn2_1a$ $20.815(5)$ $26.072(6)$ $17.128(4)$ $90$ $90$ $90$ $90$ $9298.88(12)$ $4$ $1.746$ $1.109$ $4944$ no correction $0.81/0.66$ $100(2)$ $51.48$ $42780$ $17592$ $2393, 11252$ $8450$ $0.1038$ $0.3023$ $0.1956$ $0.0000$ $0.954$ $0.758$ $28202$

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

The C<sub>60</sub> complexes with Mn(Et<sub>2</sub>dtc)<sub>2</sub> and Fe(Et<sub>2</sub>dtc)<sub>2</sub> were also obtained as powders by mixing C<sub>60</sub> (25 mg, 0.0347 mmol) and a twofold molar excess of M(Et<sub>2</sub>dtc)<sub>2</sub> in C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (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<sub>2</sub>dtc)<sub>2</sub> and Fe(Et<sub>2</sub>dtc)<sub>2</sub> 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<sup>-1</sup>). 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  $(\chi_0)$ were subtracted from the experimental values. The values of  $\Theta$ ,  $\chi_0$ were calculated using the appropriate formula:  $\chi_{\rm M} = C/(T - \Theta) +$  $\chi_0$ . 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<sup>12–10<sup>14</sup></sup> photons/cm<sup>2</sup>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<sub>a</sub> 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.<sup>[66]</sup> 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 Xray 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<sub>3</sub> groups with  $U_{iso} = 1.5 U_{eq}$ . 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  $Cu(nPr_2dtc)_2$  and complexes 11 and 13 (Tables S1 and S2, Figures S1–S7).

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