

DT-TTF salts with [Cu(dcdmp)]⁻ ; the richness of different stoichiometries

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ABSTRACT

(DT-TTF)[Cu(dcdmp)₂] (**1**), (DT-TTF)₂[Cu(dcdmp)₂] (**2**) and (DT-TTF)₃[Cu(dcdmp)₂]₂ (**3**) are three new charge transfer salts obtained by electrocrystallization of the donor DT-TTF (dithiophene-tetrathiafulvalene) with the diamagnetic copper complex [Cu(dcdmp)₂]⁻ (dcdmp=2,3-dicyano-5,6-dimercaptopyrazine). Compounds **1** and **3** crystallize in the triclinic system and consist of out-of-registry layers of mixed stacks of donor and acceptor molecules. (DT-TTF)₂[Cu(dcdmp)₂] presents a structure similar to the parent spin-ladders systems with donors stacks arranged in pairs, however a magnetic spin-ladder behavior is not observed probably due to strong interactions between pairs. Compound **3**, despite the mixed nature of the stacks, displays relatively high conductivity (7 S/cm) due to a one-dimensional network of interactions between donors.

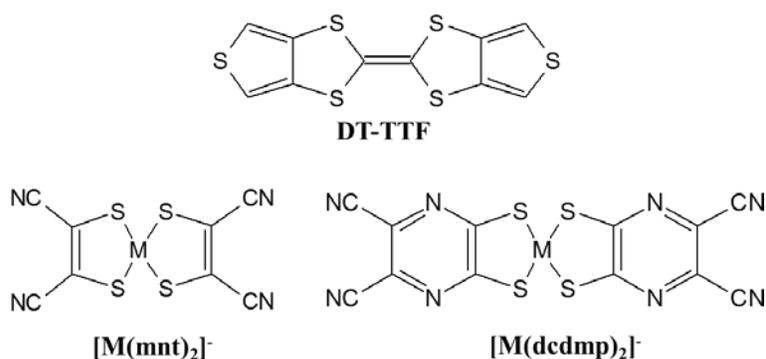
INTRODUCTION

Since the report of (DT-TTF)₂[Au(mnt)₂] (DT-TTF=dithiophene-tetrathiafulvalene and mnt= maleonitriledithiolate) as the first organic based spin-ladder system,¹⁻² there has been an increasing interest in exploring other molecule based compounds with spin-ladder behavior and several of such compounds have been described.³⁻⁵ However the molecular spin-ladder systems found so far are in most cases based on quite different molecular units with unrelated structural types. The exceptions to this situation are the compounds derived from (DT-TTF)₂[Au(mnt)₂] with relatively minor modifications in the donor or acceptor units. Spin-ladder behavior has been reported in salts with diamagnetic anions very similar to [Au(mnt)₂], such as [Cu(mnt)₂] and

[Au(*i*-mnt)₂]⁶ or based on similar thiophenic-TTF donors such as (α -DT-TTF)⁷

(α -DT-TTF=alpha-dithiophene-tetrathiafulvalene and *i*-mnt=*iso*-maleonitriledithiolate). Even so with [Cu(mnt)₂] and [Au(*i*-mnt)₂] anions, different stoichiometries and structures have been obtained in the same preparation by electrocrystallization. Larger modifications in the donor or the acceptor do not preserve the ladder structure of the donors with paired stacks and completely different structures can be obtained. For instance with pyrazinedithiolene and diselenolene ligands salts a different stoichiometry was obtained as (DT-TTF)₄[Cu(pdt)₂]₃ (pdt=pyrazinedithiolate) undergoing a series of transitions upon cooling.⁸ Several transition metal-bisdithiolene anions have been extensively used in salts with thiophenic-TTF type donors, but those based on the dcdmp (dcdmp=dicyanodimercaptopyrazine) ligand, have been a lot less explored and restricted to Au and Ni.⁹⁻¹¹ In this paper we report three new salts of DT-TTF with the [Cu(dcdmp)₂], that presents different stoichiometries, including a 2:1 salt with different mode of pairing donor stacks in the crystal structure, that does not have a magnetic spin-ladder behavior.

Scheme 1. Chemical structures of electron donor DT-TTF and metal bisdithiolene anions.



EXPERIMENTAL SECTION

General Methods. DT-TTF¹² and (n-Bu₄N)[Cu(dcdmp)₂]¹³ were prepared following previously described procedures. Electrocrystallization was performed in H-shaped two-compartment cells separated by frit glass with Pt electrodes and under galvanostatic conditions. Dichloromethane was also purified using standard procedures¹⁴ and freshly distilled immediately before its use.

Synthesis of (DT-TTF)_x[Cu(dcdmp)₂]_y (**1 (x=1, y=1); **2** (x=2, y=1); **3** (x=3, y= 2)).** Crystals of these salts were obtained by electrocrystallization, at room temperature, from a dichloromethane solution of the DT-TTF donor and the tetrabutylammonium salt of [Cu(dcdmp)₂]⁻ as electrolyte, in approximately stoichiometric amounts. The system was sealed under nitrogen and after ~10 days, using a current density of ~1.0 μA/cm², dark green needles (**1**) and black plate-shaped crystals (**2** and **3**) grown on the anode were collected, washed with dichloromethane and dried. Each electrocrystallization affords crystals of the different stoichiometries in uncontrolled proportion.

X-ray Crystallography. Selected single crystals were mounted on a loop with protective oil and X-ray data was collected on a Bruker APEX II CCD detector diffractometer using graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and operating in a φ and ω scans mode. A semi empirical absorption correction was carried out using SADABS.¹⁵ Data collection, cell refinement and data reduction were done with the SMART and SAINT programs.¹⁶ The structures were solved by direct methods using SIR97¹⁷ and refined by fullmatrix least-squares methods using the program SHELXL97¹⁸ using the winGX software package.¹⁹ Non-hydrogen atoms were refined with anisotropic thermal parameters whereas H-atoms were placed in

idealized positions and allowed to refine riding on the parent C atom. Molecular graphics were prepared using ORTEP 3.²⁰

Electrical Transport Properties. Electrical conductivity and thermopower were measured in single crystals in the temperature range of 50–320 K, using a measurement cell attached to the cold stage of a closed cycle helium refrigerator. In the first step, the thermopower was measured by using a slow AC (ca. 10^{-2} Hz) technique,²¹ by attaching two $\varnothing=25$ μm diameter 99.99 % pure Au wires (Goodfellow metals), thermally anchored to two quartz blocks, with Pt paint (Demetron 308A) to the extremities of an elongated sample as in a previously described apparatus,²² controlled by a computer.²³ The oscillating thermal gradient was kept below 1 K and was measured with a differential Au-0.05 at. % Fe vs. chromel thermocouple of the same type. The absolute thermoelectric power of the samples was obtained after correction for the absolute thermopower of the Au leads, by using the data of Huebner.²⁴

EPR Measurements. The EPR spectra were obtained using a Bruker ELEXYS E500 and Bruker ESP-300 E X band spectrometers equipped with a field-frequency (F/F) lock accessory and a built in NMR Gaussmeter. A rectangular TE102 cavity was used for the measurements. The signal to noise ratio of spectra was increased by accumulation of scans using the F/F lock accessory to guarantee large field reproducibility. Precautions to avoid undesirable spectral distortions and line broadenings, such as those arising from microwave power saturation and magnetic field over modulation, were also taken into account. To control the temperature in the range 4–300 K an Oxford ESR-900 cryostat was used.

RESULTS AND DISCUSSION

From the electrocrystallization of the DT-TTF donor in the presence of the tetrabutylammonium salt of $[\text{Cu}(\text{dcdmp})_2]^-$ three compounds, with different donor-acceptor stoichiometries, were isolated. Obtaining salts with different stoichiometries from one electrocrystallization is not unprecedented for compounds based on the donor DT-TTF since, for instance with the anion $[\text{Cu}(\text{mnt})_2]^-$, at least two salts (2:1 and 1:1) could be characterized.⁶ With $[\text{Au}(\text{dcdmp})_2]$ and $[\text{Ni}(\text{dcdmp})_2]$ salts mixed stack structures have been obtained with donor: acceptor stoichiometries of 3:2 and 2:1, respectively.⁹ In the present work single crystals of (DT-TTF) $[\text{Cu}(\text{dcdmp})_2]$ (**1**), (DT-TTF)₂ $[\text{Cu}(\text{dcdmp})_2]$ (**2**) and (DT-TTF)₃ $[\text{Cu}(\text{dcdmp})_2]$ ₂ (**3**) with quality and size suitable for X-ray diffraction, electrical transport and magnetic properties measurements could be isolated from the same preparation. Crystal and structural refinement data, for compounds **1-3**, are listed in Table 1.

Compound **1** crystallizes in the triclinic system, space group P-1. The asymmetric unit contains one DT-TTF donor molecule and one $[\text{Cu}(\text{dcdmp})_2]^-$ anion, both at general positions (Table S1, S2). The donor molecule is, within experimental error, essentially planar. The transition metal anion shows a very small tetrahedral distortion of the coordination by sulfur atoms (Figure 1).

Table 1. Crystal and refinement data for (DT-TTF)[Cu(dcdmp)₂] (**1**) (DT-TTF)₂[Cu(dcdmp)₂] (**2**) and (DT-TTF)₃[Cu(mnt)₂]₂ (**3**)^a

Compound	(DT-TTF) [Cu(dcdmp) ₂] (1)	(DT-TTF) ₂ [Cu(dcdmp) ₂] (2)	(DT-TTF) ₃ [Cu(dcdmp) ₂] ₂ (3)
Formula	C ₂₂ H ₄ CuN ₈ S ₁₀	C ₃₂ H ₈ CuN ₈ S ₁₆	C ₅₄ H ₁₂ Cu ₂ N ₁₆ S ₂₆
Molec. mass	764.47	1080.96	1845.44
T (K)	150(2)	150(2)	150(2)
Dimens. (mm)	0.25×0.15×0.10	0.30×0.10×0.03	0.40×0.30×0.08
Crystal color	Black	Dark green	Black
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	P-1	P2 ₁ 2 ₁ 2	P-1
<i>a</i> (Å)	8.7517 (2)	22.8964(6)	9.9810(2)
<i>b</i> (Å)	11.6930(3)	29.1651(8)	12.7513(2)
<i>c</i> (Å)	13.9624(4)	5.66990(10)	15.4285(3)
α (°)	68.6620(10)	90.00	101.3860(10)
β (°)	82.3290(10)	90.00	106.493(2)
γ (°)	83.4370(10)	90.00	112.389(3)
Volume (Å ³)	1315.62(6)	3786.22(16)	1634.22(5)
Z	2	4	1
ρ_{calc} (g.cm ⁻³)	1.930	1.896	1.875
h, k, l range	±10, -13/+14, -16/+17	±27, -35/+33, ±6	-11/+12, ±15, ±18
θ_{max} (°)	25.68	25.35	25.68
Refl. collected	16646	46038	23994
Refl. indexed	4508	6918	6162
Refl. >2 σ (I)	3791	6151	5552
R1	0.0292	0.0372	0.0240
ω R2	0.0710	0.0842	0.0636

^a Crystallographic data (excluding structure factors) for **2**, **1** and **3** were deposited with the Cambridge Crystallographic Data Centre with nos. CCDC 1470410-1470412, respectively.

Compound **3** crystallizes in the triclinic system, space group P-1. The unit cell is composed by one anion [Cu(dcdmp)₂]⁻, at general position, and two DT-TTF donor molecules, molecule A at

an inversion center and molecule B at general position (Table S1, S2). This compound presents the same packing pattern of the previously described compound (DT-TTF)₃[Au(dcdmp)₂]₂ composed of an out-of-registry alternated packing of donor trimers (BAB) and anion dimers.⁹ While the donor molecule B and the monoanion present a small boat type distortion the donor molecule A is essentially planar (Figure 2).

Based on an analysis of the central C=C and C-S bond lengths of the donor it is possible to conclude that molecule B in **3** is partially oxidized, with electric charge close to +0.5, while molecule A in **3** and the donor molecule in **1** are fully oxidized (Table S3). In both compounds **1** and **3**, the bond lengths of the electronic acceptor unit, [Cu(dcdmp)₂], are identical to those previously reported for this monoanionic complex¹³ and within the range found in related square planar monoanionic copper complexes (Table S4).

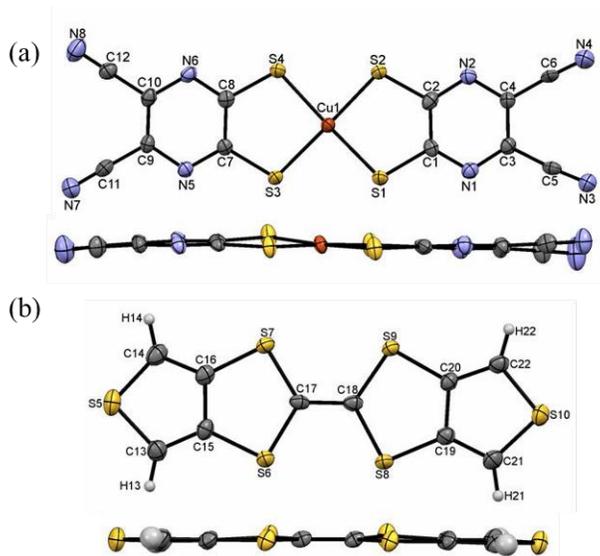


Figure 1. ORTEP and atomic numbering scheme of compound **1**, with thermal ellipsoids at 70 % probability level.

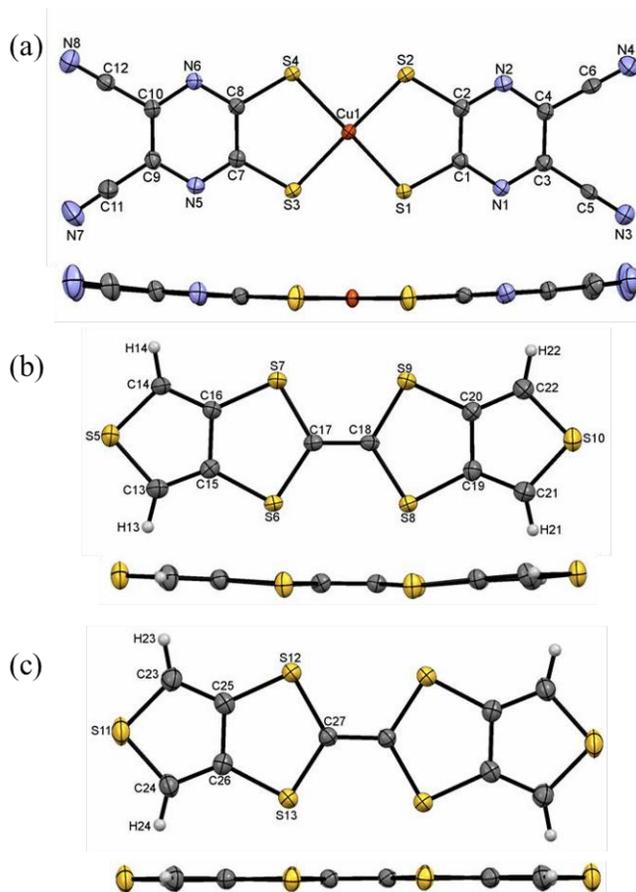


Figure 2. ORTEP and atomic numbering scheme of compound **3**, with thermal ellipsoids at 70 % probability level: b) donor molecule B and c) donor molecule A.

In spite of the different stoichiometries, the crystal structures of compounds **1** and **3** are similar sharing a common packing pattern consisting of mixed stacks of donor and acceptor molecules. The structures are composed by mixed stacks, along $a+b$, of pairs of anions alternating with pairs of cations ($D^+D^+A^-A^-D^+D^+$) in the case of **1** or cation trimers in the case of **3** ($\dots D^{+0.5}D^{+1}D^{+0.5} A^-A^-D^{+0.5}D^{+1}D^{+0.5} \dots$) (Figure 3). Compound **3** displays a crystal pattern very similar to that previously found in $(DT-TTF)_3[Au(dcdmp)_2]_2$ (Figure 3b₂).⁹ In both compounds **1** and **3**, the mixed stacks are arranged out of registry in layers along the a,b plane and neighboring layers are slightly displaced, along c , as illustrated in Figure 3a₃/b₃.

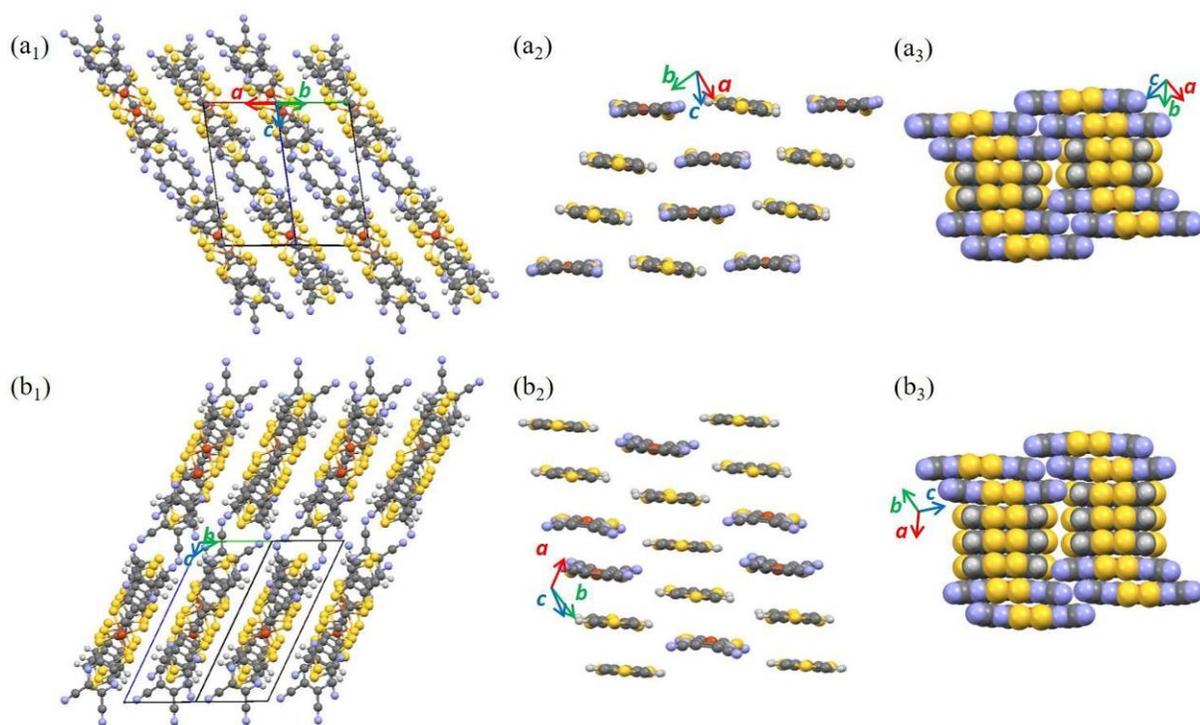


Figure 3. Crystal structure of: (a) (DT-TTF)[Cu(dcdmp)₂] (**1**) and (b) (DT-TTF)₃[Cu(dcdmp)₂]₂ (**3**) viewed along $a+b$. (a₁, b₁) Partial views along the long axis of the molecules of neighboring stacks in the same layer (a₂, b₂). Partial view between stacks in different layers along the molecular short axis (a₃, b₃).

In both compounds the DT-TTF molecules present the usual overlapping mode, virtually identical, with a small displacement along the molecule short axis (Figure 4a and 4b) with interplanar distances of 3.407 and ~ 3.524 Å in **1** and **3**, respectively. There are several short S \cdots S contacts, involving both the TTF core and the thiophenic-sulfur atoms. The overlapping mode of the anions (Figure 4) is also identical in both compounds and is characterized by a large displacement of the Metal over one of the atoms in the dithiolenic C=C double bond. There are no short interactions between anions within the pair, which are separated by interplanar distances of

3.31 Å (in **3**) and 3.39 Å (in **1**), nor between the dicationic trimers/dimers and the pairs of anions along the stacks. Nevertheless there are side-by-side S \cdots S and S \cdots N short contacts between cations and anions in the same layer, in the *a,b* plane, and rather short C-H \cdots S hydrogen bonds between cations and anions in neighboring layers (Table S5, S6).

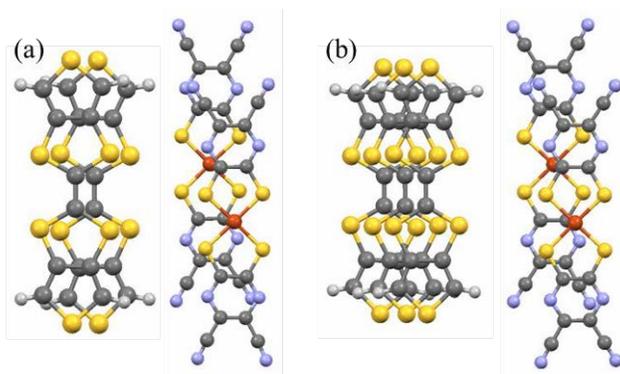


Figure 4. Donor-Donor (left) and Acceptor-Acceptor (right) overlap modes in (a) (DT-TTF)[Cu(dcdmp)₂] (**1**) and (b) (DT-TTF)₃[Cu(dcdmp)₂]₂ (**3**).

(DT-TTF)₂[Cu(dcdmp)₂] (**2**) crystallizes in the orthorhombic space group P2₁2₁2. The asymmetric unit is composed by two (DT-TTF)^{+0.5} donor molecules, A and B, and one monoanionic molecule of [Cu(dcdmp)₂]⁻, both at general positions (Table S1). One of the donor molecules is essentially planar, within experimental error, but the other donor molecule as well as the copper complex present a slight boat type distortion (Figure 5).

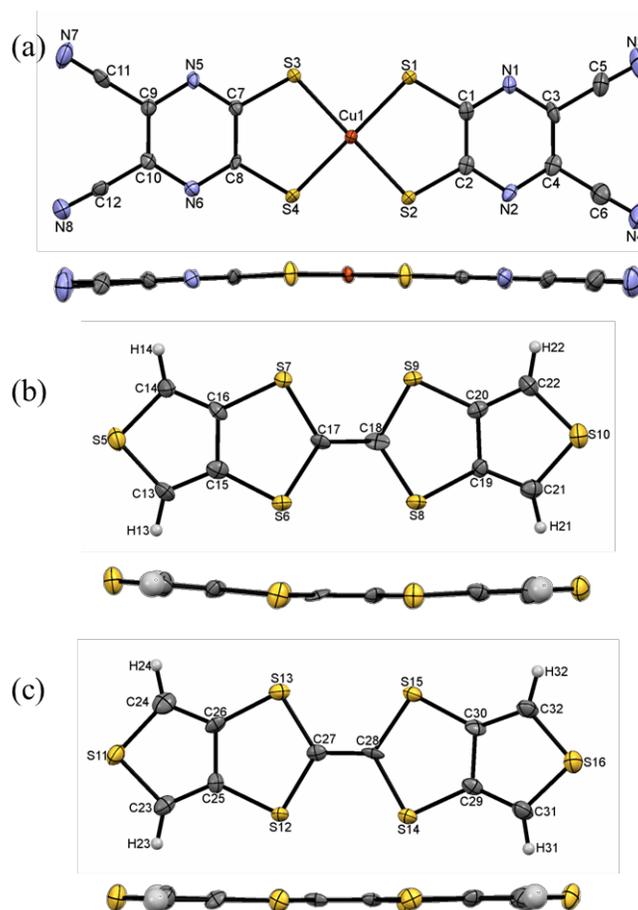


Figure 5. ORTEP and atomic numbering scheme of compound **2**, with thermal ellipsoids at 70 % probability level.

The bond lengths of the [Cu(dcdmp)₂] complex in **2** are identical to those of compounds **1** and **3** described above and those previously found in a salt of the monoanionic complex¹³ (Table S2). The C-S and C=C bond lengths of the two donors A and B in **2** are identical to each other (1.745 and 1.361/ 1.745 and 1.372 Å respectively) and to the partially oxidized donor molecule B in **3**. These results are consistent with a partial oxidation (DT-TTF)^{+0.5} of both donor units (Table S3).

The crystal structure of **2** is composed by segregated regular stacks of donor and acceptors units along the *c*-axis (Figure 6a, c). In the *a,b* plane, perpendicular to the stacking axis, there are pairs

of closely interacting stacks of segregated donors molecules A and B, alternating with acceptor stacks, in a packing pattern similar to that found in molecular spin-ladder systems derived from this donor and closely related ones.^{1,6-7,25-26} However when compared to these spin-ladder systems the molecules in the crystal structure of **2** present more pronounced tilting of $\sim 30.5^\circ$ towards the stacking axis (Figure 6). Also, along the stacks, the interplanar distances, between the donor molecules (2.760 Å, 2.777 Å) and the acceptor units (3.006 Å) are much smaller than those found in (DT-TTF)₂[Cu(mnt)₂] compound (3.549 Å and 3.489 Å, respectively).⁶

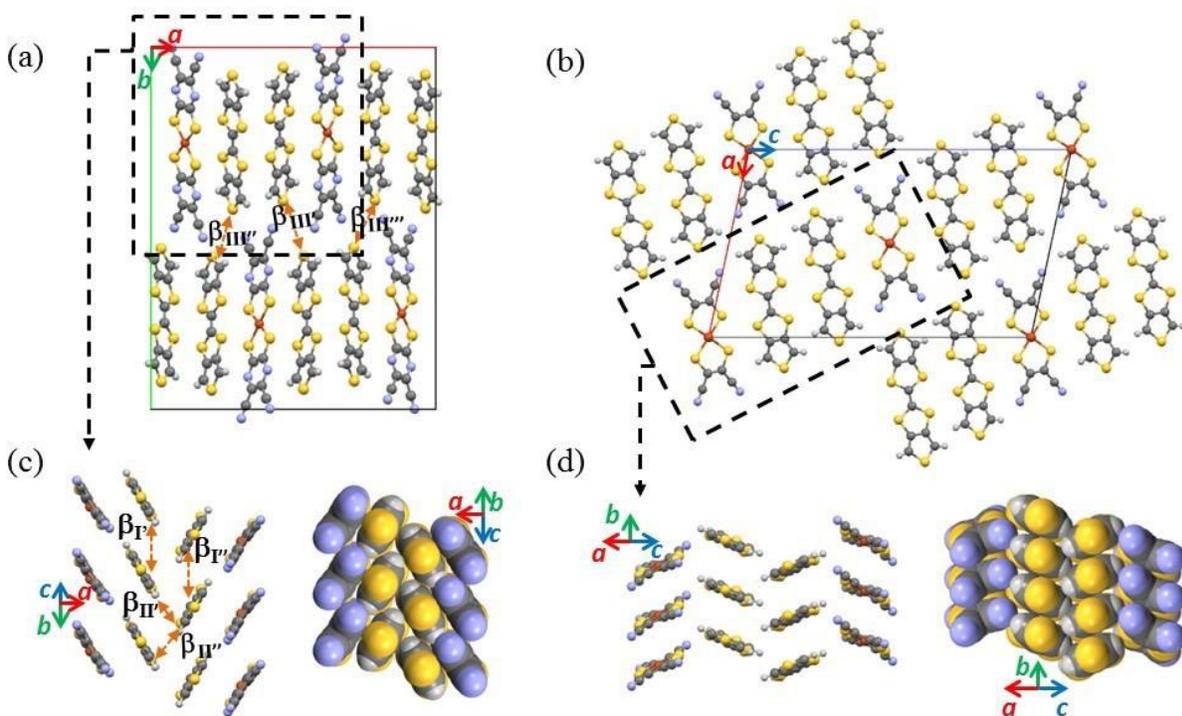


Figure 6. Crystal structure of: (a) (DT-TTF)₂[Cu(dcdmp)₂] (**2**) and (b) (DT-TTF)₂[Cu(mnt)₂]⁶ viewed along the stacking axis *c* and *b* respectively. Partial view of one layer of neighboring stacks in compound **2**(c), and (DT-TTF)₂[Cu(mnt)₂] (d). The different interactions β between donor molecules are indicated.

The donor stacks are composed uniquely by one of the two distinct DT-TTF molecules A or B. Although crystallographic inequivalent these molecules have identical geometrical parameters. There are several short S··S contacts between donor molecules denoting strong intermolecular interactions: along the stacks through S14··S15 (3.568 Å), S12··S13 (3.657 Å) and S6··S7 (3.618 Å), S8··S9 (3.582 Å) while between the stacks through S6··S13 (3.598 Å) and S8··S15 (3.630 Å) (Table S7). In addition the peripheral thiophenic sulfur atoms of donors in different pairs connect through S10··S10* short contacts (3.629 Å). Acceptor molecules are also connected by two short interstack S1··S2 and S3··S4 contacts. Furthermore there are several short contacts between donor and acceptor molecules including S··N and N··H-C hydrogen bonds (Table S7).

Different intermolecular contacting modes can be seen in the structure of **2** when compared with the related molecular spin-ladder compound (DT-TTF)₂[Cu(mnt)₂] (Figure 7). Due to the acute tilting of the molecules in compound **2**, the intrastack contacts result from side-by-side interactions, since the molecules are much more displaced along the molecular shorter axis than in the related spin-ladder systems. For this same reason, the donor interstack is favored leading to stronger interactions due to the distance shortening between donors in paired stacks (angle between molecules in the neighboring stacks 60.9 °). Moreover [Cu(dcdmp)₂]⁻ molecules presents a larger displacement along the molecule shorter axis, than the observed in the overlapping mode found in [Cu(mnt)₂]⁻ (Figure 7).

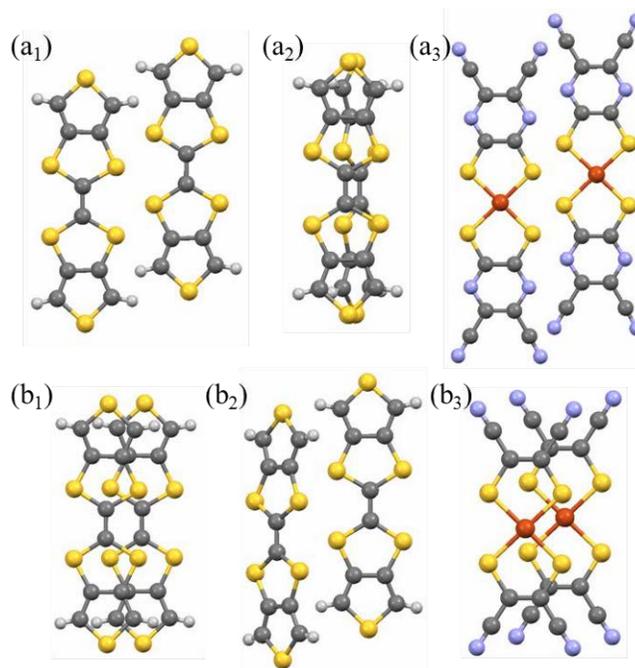


Figure 7. Donor-donor contact modes in compound **2** (a) and in (DT-TTF)₂[Cu(mnt)₂] (b) between interstacks (a₁, b₁), intrastacks (a₂, b₂) and between anion-anion (a₃, b₃).

In the structure of **2** there are seven distinct intermolecular donor-donor interactions; two between donors along the stacks of molecules A(β_{I}) and B (β_{I}) respectively, two between molecules A and B in paired stacks (β_{II} and β_{II}) and three between stacks in different pairs (β_{III} , β_{III} and β_{III}) (Figure 6a and 6c). These seven distinct interactions in **2**, due to the non-equivalency of the stacks in a pair, contrast with the only three distinct interactions found in the related spin ladder systems, where the stacks are equivalent and related by a screw axis. These interactions between neighboring donor units were estimated by calculations based on the extended Hückel approximation using a double- ξ basis.²⁷⁻³⁰ In spite of the uncertainty on the absolute values obtained by the theoretical calculations under this approach, the results provide a fair indication of their relative magnitude (Table 2).

Table 2. Intermolecular interactions β_{I-VII} (meV) between donor units calculated using the extended Hückel approximation and a double- ξ basis set in $(\alpha\text{-DT-TTF})_2[\text{Au}(\text{mnt})_2]$, $(\text{DT-TTF})_2[\text{Au}(\text{mnt})_2]$, $(\text{DT-TTF})_2[\text{Cu}(\text{mnt})_2]$ and $\text{DT-TTF}_2[\text{Cu}(\text{dcdmp})_2]$ (**2**).

	β_{I}	$\beta_{\text{I}'}$	β_{II}	$\beta_{\text{II}'}$	β_{III}	$\beta_{\text{III}'}$	$\beta_{\text{III}''}$
$(\alpha\text{-DT-TTF})_2[\text{Au}(\text{mnt})_2]$ ⁷	49.4	---	77.0	---	5.4	---	---
$(\text{DT-TTF})_2[\text{Au}(\text{mnt})_2]$	104.6	---	66.3	---	15.3	---	---
$(\text{DT-TTF})_2[\text{Cu}(\text{mnt})_2]$	104.2	---	74.3	---	16.6	---	---
$\text{DT-TTF}_2[\text{Cu}(\text{dcdmp})_2]$ (2)	206.1	206.8	53.7	-209.1	3.9	2.0	-4.8

As it can be seen in Table 2 the interactions calculated for the isostructural salts $(\alpha\text{-DT-TTF})_2[\text{Au}(\text{mnt})_2]$, $(\text{DT-TTF})_2[\text{Au}(\text{mnt})_2]$, $(\text{DT-TTF})_2[\text{Cu}(\text{mnt})_2]$ and compound **2**, show that the $[\text{Cu}(\text{dcdmp})_2]$ salt presents the highest interactions along the chains (β_{I} and $\beta_{\text{I}'}$). Furthermore one of the interactions between donors in paired stacks ($\beta_{\text{II}'}$) shows also a rather high value in the same magnitude than β_{I} and $\beta_{\text{I}'}$. The interaction between stacks in different pairs (β_{III} , $\beta_{\text{III}'}$ and $\beta_{\text{III}''}$) are small and comparable to that of the $(\alpha\text{-DT-TTF})_2[\text{Au}(\text{mnt})_2]$ salt which was found to be a rather small interaction and magnetically irrelevant in the $\alpha\text{-DT-TTF}$ salts.^{2,7} However in compound **2** there are more interactions connecting nearby pairs of stacks in all directions in the a,b plane perpendicular to the chains, making possible a 3D coupling between donors.

Figures 8 and 9 present the electrical resistivity, ρ , and thermoelectric power, S , measured as a function of temperature in single crystals of **2** and **3** that show different semiconducting behaviors. Compound **2** presents a slightly higher conductivity value $\sigma_{\text{RT}} \sim 30$ S/cm at room temperature with a quite small activation energy of 45 meV at room temperature. Upon cooling there is a relatively

sharp anomaly in the activation energy with a sharp maximum in the slope $\ln\sigma/d(1/T)$ at 205 K indicating the onset of a transition, reminiscent to those observed in $(DT-TTF)[M(mnt)_2]$ compounds, with $M=Au, Cu$,⁶ specially the last one where this transition is more sharp and it was recently shown to be associated with a charge ordering in the donor chains.²⁶ This change of regime is also observed in thermopower, which at higher temperatures has an almost metallic regime with $S_{RT}= 60 \mu V/K$ decreasing almost linearly with temperature until ~ 220 K, and below this temperature it has a clear change to faster decrease following a typical semiconducting regime.

Compound **3** presents also a semiconducting regime of the electrical transport properties, with $\sigma_{RT}\sim 7$ S/cm at room temperature and an almost constant activation energy of 135 meV.

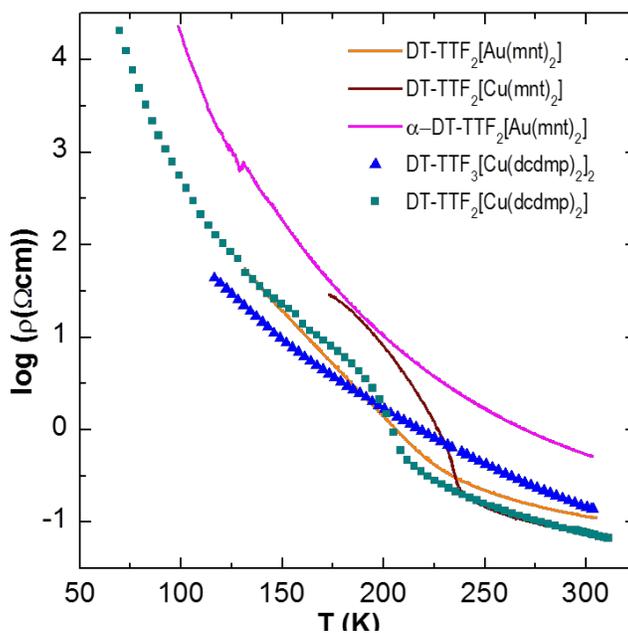


Figure 8. Electrical resistivity of single crystals of $(DT-TTF)_x[Cu(dcdmp)_2]_y$ family and related compounds, as a function of temperature.

The thermoelectric power of **3**, as shown in Figure 9, is $\sim 50 \mu\text{V/K}$ at room temperature, decreasing upon cooling approximately proportionally to $1/T$ with a behavior indicative of a semiconducting regime in agreement with the electrical conductivity.

The relatively high conductivity of **3** in spite of the mixed stacked nature of the structure can be understood as a result of the strong interaction between donor trimers along a , establishing a distorted 1D chain of donors A and B ($\dots B^{0.5+}A^{0.5+}B^{0.5+}A^{0.5+}B^{0.5+}A^{0.5+} \dots$) with strong interactions (Figure 10).

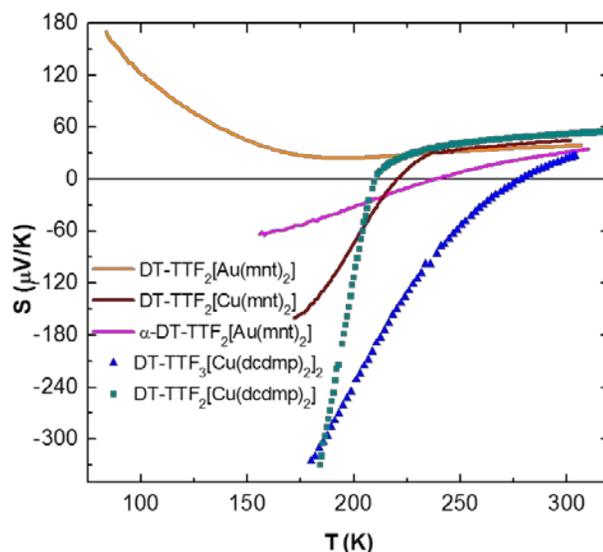


Figure 9. Thermoelectric power of $(\text{DT-TTF})_x[\text{Cu}(\text{dcdmp})_2]_y$ family and related compounds as a function of temperature.

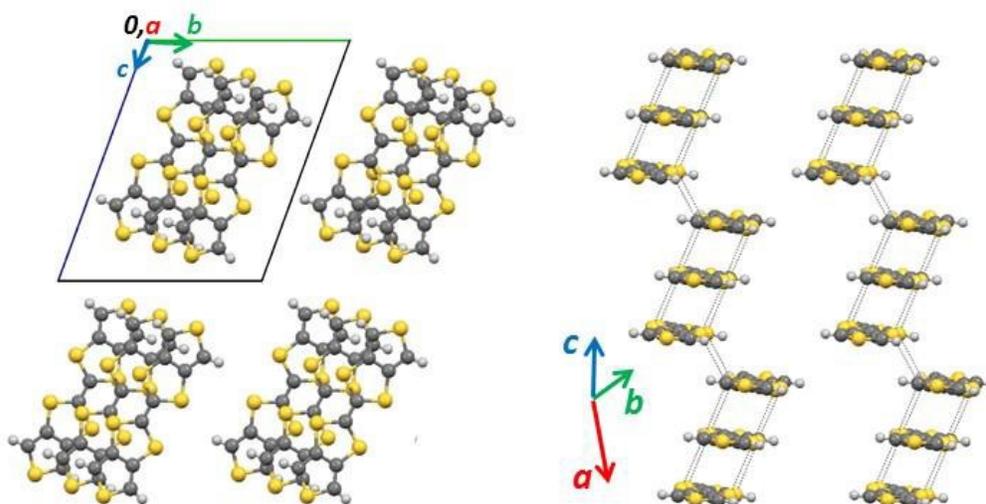


Figure 10. DT-TTF units in the crystal structure of **3** seen along a (left) and a partial view perpendicular to a along the donors long axis (right). The thin lines denote a chain of short contacts between donors arranged in trimers.

The presence of more than one phase in one electrocrystallization preparation makes it unfeasible magnetic measurements in polycrystalline samples. However the spin susceptibility could be obtained using EPR measurements in selected crystals. EPR spectra consist, at room temperature, in a single line 28.7 G wide and centered at g -value of 2.0058, typical of the organic donor as expected in view of the diamagnetic nature of the anions.

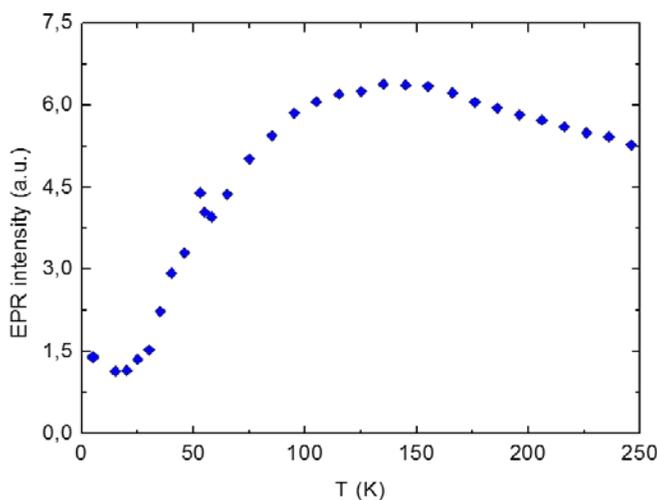


Figure 11. EPR spin susceptibility of $(\text{DT-TTF})_2[\text{Cu}(\text{dcdmp})_2]$ (**2**) as a function of temperature T.

The spin susceptibility obtained by double integration of EPR spectra of the selected crystals as a function of temperature is shown in Figure 11. Upon cooling, there is first a small increase of the spin susceptibility, with a broad maximum at circa 135 K followed by a faster decrease toward zero with a small Curie tail below 20 K. However this decrease is not regular and at ~ 53 K there is an anomaly, seen as a small but sharp peak, associated with a drastic linewidth change and there is also noticed a faster decrease of susceptibility below 40 K. The general behavior of the temperature dependence of the susceptibility apart from this ~ 53 K anomaly could be seen as similar to the related spin-ladder compounds previously discussed.⁶ However it could not be fitted to a spin-ladder model and the existence of the anomaly at 53 K clearly indicates that $(\text{DT-TTF})_2[\text{Cu}(\text{dcdmp})_2]$ (**2**) is not a spin-ladder system in spite of the double chain structure of the donors. While the clarification of the nature of the magnetic transition at 53 K requires further studies it is worth noting that comparing the structure of **2** with the other spin-ladder systems we expect a stronger interchain interaction. In fact in **2** each donor chains

interacts with two neighboring ones making a 2D network of transverse interactions between the paired stacks in the *a,b* plane, while in the spin-ladder systems like (DT-TTF)₂[Au(mnt)₂], these interactions between chains are restricted to only one direction. Most likely the 2D nature of transverse interactions in **2** is enough to destroy the spin liquid behavior favoring instead a 3D ordering arrangement of the spins.

CONCLUSION

In summary salts with three different donor:acceptor stoichiometries 1:1 (**1**), 2:1 (**2**) and 3:2 (**3**), were obtained by combination of the donor DT-TTF with [Cu(dcdmp)₂] anion. The 2:1 salt (DT-TTF)₂[Cu(dcdmp)₂] (**2**) presents a new type of arrangement of donors as paired stacks of strongly tilted molecules, however without a spin-ladder behavior probably due to strong interactions between pairs. Compounds **1** and **3** present a structure composed by mixed stacks of acceptor dimers alternating with donor dimers or trimers, respectively. In spite the alternated nature of these stacks in compound **3** displays relatively high conductivity due to a one dimensional network of interactions between donors.

ASSOCIATED CONTENT

Supporting Information. Tables of bond lengths and short contacts in the compounds: (DT-TTF)[Cu(dcdmp)₂] (**1**), (DT-TTF)₂[Cu(dcdmp)₂] (**2**) and (DT-TTF)₃[Cu(dcdmp)₂]₂ (**3**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

DT-TTF, dithiophenetetrathiafulvalene; mnt, maleonitriledithiolate; dcdmp, 2,3-dicyano-5,6-dimercaptopyrazine, TTF, tetrathiafulvalene; α -DT-TTF, alpha-dithiophene-tetrathiafulvalene; *i*-mnt, *iso*-maleonitriledithiolate; pdt, pyrazinedithiolate.

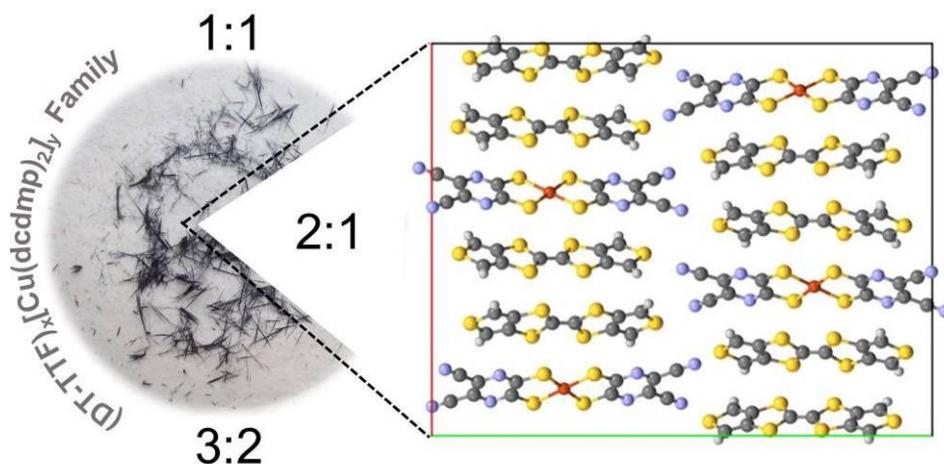
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Table of Contents Graphic and Synopsis



Three new charge transfer salts of the family $(\text{DT-TTF})_x[\text{Cu}(\text{dcdmp})_2]_y$, **1** ($x=y=1$), **2** ($x=2, y=1$) and **3** ($x=3, y=2$), were prepared. Despite of the spin-ladder like crystal structure, **2** does not display magnetic spin-ladder behavior. On the other hand **3** has relatively high room temperature conductivity (7 S/cm) despite its crystal structure being composed by donor-acceptor mixed stacks.