

Article

Structural and Electrical Properties of the τ -(P-S,S-DMEDT-TTF)₂ (AuCl₂)_y Compound with ($y \approx 0.9$)

Vassilis Psycharis ^{1,*}, George A. Mousdis ², Keizo Murata ³ and George C. Papavassiliou ²

¹ Institute of Advanced Materials, Physicochemical Processes, Nanotechnology and Microsystems, Department of Materials Science, National Centre for Scientific Research (NCSR) “Demokritos”, Aghia Paraskevi Attikis 153 10, Greece

² Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens 11635, Greece; E-Mails: gmousdis@eie.gr (G.A.M.); pseria@eie.gr (G.C.P.)

³ Department of Physics, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan; E-Mail: muratak@sci.osaka-cu.ac.jp

* Author to whom correspondence should be addressed; E-Mail: vpsychar@ims.demokritos.gr; Tel.: +30-210-650-3346; Fax: +30-210-651-9430.

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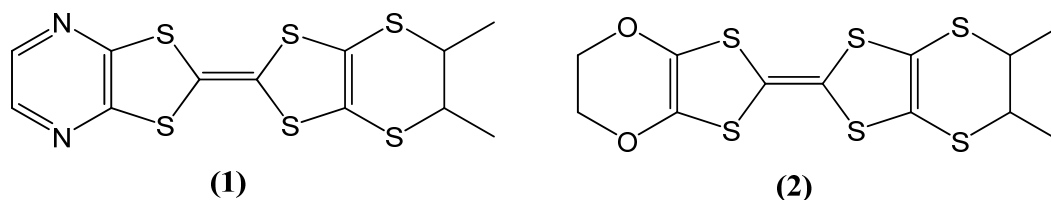
Abstract: The compound τ -(P-S,S-DMEDT-TTF)₂(AuCl₂)_y (where P-S,S-DMEDT-TTF is the compound pyrazino-(S,S)-dimethyl-ethylenedithio-tetrathiofulvalene) crystallizes in the non-centrosymmetric space group *I*-42*d*, with $a = 7.3260(1)$ Å and $c = 67.5487(12)$ Å (RT data) and remains tetragonal in the temperature range from RT to 100 K. This compound is a quasi-two-dimensional material and the relation of the lattice of the order part of the structure created by the donor molecules with that of the disordered anion lattice revealed by intense diffusion streaks give a value of $y \approx 0.9$. In contrast to the Br and I analogs or the related compounds which contain the compound ethylenedioxy-S,S-dimethylenedithiotetrathiafulvalene (abbreviated as EDO-S,S-DMEDT-TTF) as donor and which exhibit anisotropic metallic behavior down to low temperature, this compound is anisotropic semiconductor in the same temperature range. The appearance of satellites on the diffraction images recorded below 110 K indicates a structural change. Resistivity measurements show that this material is a semiconductor with anisotropy σ_a/σ_c of ca. 400–1400 at room temperature.

Keywords: organic semiconductor; quasi-two-dimensional; crystal structure; diffusion intensity; low temperature diffraction

1. Introduction

During recent years, a number of τ -phase conductors based on P-SS-DMEDT-TTF(**1**) and EDO-SS-DMEDT-TTF(**2**) molecules (Figure 1) have been prepared and studied (see references [1–11]). Their general formulas are τ -(P-S,S-DMEDT-TTF)₂(AuX₂) (AuX₂)_y (abbreviated as **1X**) and τ -(EDO-S,S-DMEDT-TTF)₂(AuX₂) (AuX₂)_y (abbreviated as **2X**) with X = Cl, Br, I and $y \sim 0.75$. P-S,S-DMEDT-TTF stands for pyrazino-(S,S)-dimethyl-ethylenedithio-tetrathiofulvalene and EDO-S,S-DMEDT-TTF for ethylenedioxy-S,S-dimethylenedithiotetrathiafulvalene. Crystals of these complexes are composed of layers consisting of organic cation radicals and ordered linear anions (AuX₂), forming a unit cell of the tetragonal system. These layers are separated by disordered anions (AuX₂)_y (see [1–3]). The value of y determines the area of the Fermi surface (FS), which decreases with increasing binding. A star shaped Fermi surface results from the fourfold symmetry of the molecules packing. While the a - b plane is metallic (conducting) the interplane electrical transport displays an unusual nonmetallic behavior over the whole temperature range. This behavior contrast with what is observed in most quasi-two-dimensional (Q2D) organic compounds, where a T^2 behavior at low T , is followed by a nonmetallic behavior at higher temperatures. Except for the anisotropic conductivity, these quasi-two-dimensional (q-2D) organic–inorganic hybrid systems exhibit some other interesting phenomena, including weak ferromagnetic behavior, large negative magnetoresistance, giant Shubnikov-de Hass oscillations, a plateau of Hall resistance reminiscent of quantum Hall-effect, and chiral surface states. Crystals of **2X**, **1Br** and **1I** exhibit anisotropic metallic behavior down to low temperature values. **1Br** and **1I** [1] at around 4 K show a resistivity minimum associated with a maximum value of the mean free path of charge carriers and negative magnetoresistance which are usually considered as signatures of weak localization effect in 2D electronic systems and have been attributed to probable structural disorder. In the **2Br** system, in addition to the semiconducting behavior below 50 K, Shubnikov-de Hass oscillations with two different frequencies have been observed and have been considered as a prediction of the existence of two FSs which is probably explained with a $2a \times 2b$ lattice transformation of the unit cell [9]. In addition, from a systematic study of **2Br** a dependence of band filling and of the electric properties on heat treatment of samples with all the measured samples has been revealed to show a $2a \times 2b$ supercell, as well as aging dependence of the electric properties for **2I** [4]. Taking into account the dependence of the properties on the structure of these type of materials, a structural and electrical properties study of τ -(P-S,S-DMEDT-TTF)₂(AuCl₂) (AuCl₂)_y (abbreviated as **1Cl**) compound is presented in this paper. In contrast to other compounds **2X**, **1Br** and **1I**, this compound exhibits anisotropic semiconducting behavior down to low temperatures.

Figure 1. Two modifications of the *S,S*-dimethyl-bis(ethylene)dithio-tetrathiafulvalene molecule. Two of sulfur atoms of the ethylenedithio moiety have been replaced by nitrogen in (1) and oxygen in (2).



2. Results and Discussion

2.1. Crystal Structure and Diffusion Scattering

The synthesis and the crystallization of the compound **1**Cl have been performed by the usual electrochemical oxidation method which is further described in [1]. As referred in the experimental section, data collection with the Rigaku R-AXIS SPIDER Image Plate diffractometer using graphite monochromated radiation have revealed, in addition to the Bragg peaks, diffusion streaks characteristic for a series of these type of compounds and especially for those containing linear metal halides [12,13]. The compound **1**Cl crystallizes in the non centrosymmetric space group, *I*-42*d* and is isostructural with the **1**Br analogue [1]. The unit cell contains eight donor molecules **1**, 4 ordered anions and approximately other 3.5 anions in disordered positions, with an arrangement characteristic of the τ -phase [9]. More specifically the features of the diffuse streaks and the spots on them resemble that of τ -(EDO-*S,S*-DMEDT-TTF)₂ (AuBr₂)₁ (AuBr₂)_{*y*} [10]. The ordered part of the structure consists of a 2D layer [parallel to the (001) plane] formed by the donor molecules with their long axes parallel and their average plane normal to each other, forming in this way the characteristic tetragonal lattice of τ -phase (Figure 2). There are intermolecular contacts (Table 1, Figure S1) of S⋯S type in the range from 3.478 Å to 3.523 Å and one S⋯N type of 3.311 Å at RT, which are smaller than or close to the sum of the Van der Waals radii (3.70 Å and 3.35 Å respectively). The values of S⋯S contacts at 260 K are smaller (3.463 Å–3.512 Å) and that of S⋯N contact is slightly higher (3.33 Å). The ordered anions reside in the cavities of the tetragonal donor lattice (Figure 2). Calculations of difference Fourier maps during the structure solution process give electron density with appreciable values to be spread along the *a* or *b* crystallographic axis and in between the 2D donor layers, which is possible to be modeled with disordered AuCl₂ anions, “smeared” all along the *b* axis as in the case of the anions in other τ -phases [11]. As is mentioned in [10], these disordered chains of AuCl₂ anions are the origin of the intense diffusion streaks which are recorded on the diffraction images (Figure 3).

The spots observed on the diffusion streaks which are normal to *a** or *b** reciprocal cell axes respectively, (Figure 3a) have been interpreted [10] as two independent reciprocal lattices which are related by a 2 fold axis normal to the plane of the image of Figure 3a. As it is easily recognized by the arrangement of spots in white circles (Figure 3a), the extinction rule is that of a face-centered lattice. The two lattices of the anions have dimensions (8.1/7.33) *a* (=1/*a*’*) × 2*b* (=1/*b*’*) *b* or 2*a* × (8.1/7.33) *b*, and if there are no defects of anions in both lattices the *y* value of the disordered anions per formula unit is ≈0.9 (=7.33/8.1). Figure 3b shows the diffusion streaks as they have been recorded when the

X-ray beams falls on the crystal parallel to the a^* axis and the arrangement of the spots on them supports the interpretation of a face centered lattice.

Figure 2. Arrangement of donor molecules in the 2D layer as seen almost parallel to the c axis. The dotted lines indicate the S...S and S...N intermolecular contacts. The positions of ordered AuCl_2^- anions are also shown.

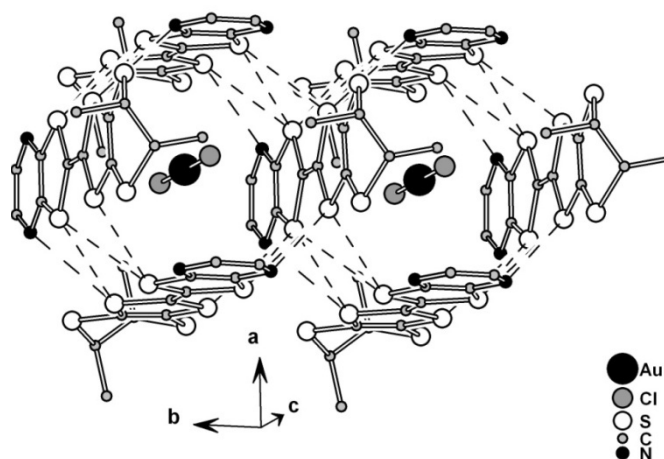


Table 1. S...S and S...N intermolecular contacts. (For the numbering scheme of atoms see Table-S1 and Figure-S1, supplementary material).

Intermolecular contacts	RT Length (Å)	260 K Length (Å)
S(2)...N(1) †,*	3.311(9)	3.33(1)
S(2)...S(3) †,*	3.478(3)	3.469(3)
S(3)...S(3) †,*	3.523(3)	3.512(3)
S(3)...S(2) †,*	3.483(3)	3.463(3)

* Symmetry transformations used to generate equivalent atoms; † : $-y, 1+x, -z$.

Figure 3. Diffusion streaks recorded on diffraction images with the X-ray beam parallel to the c^* reciprocal lattice axis, (a) and parallel to the a^* reciprocal lattice axis, (b).

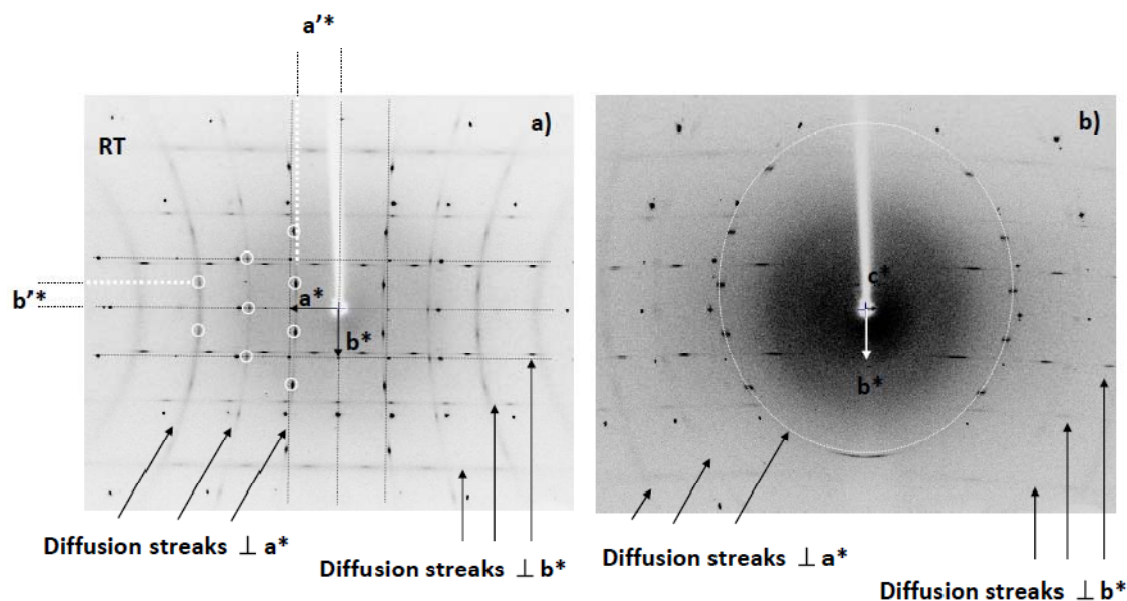
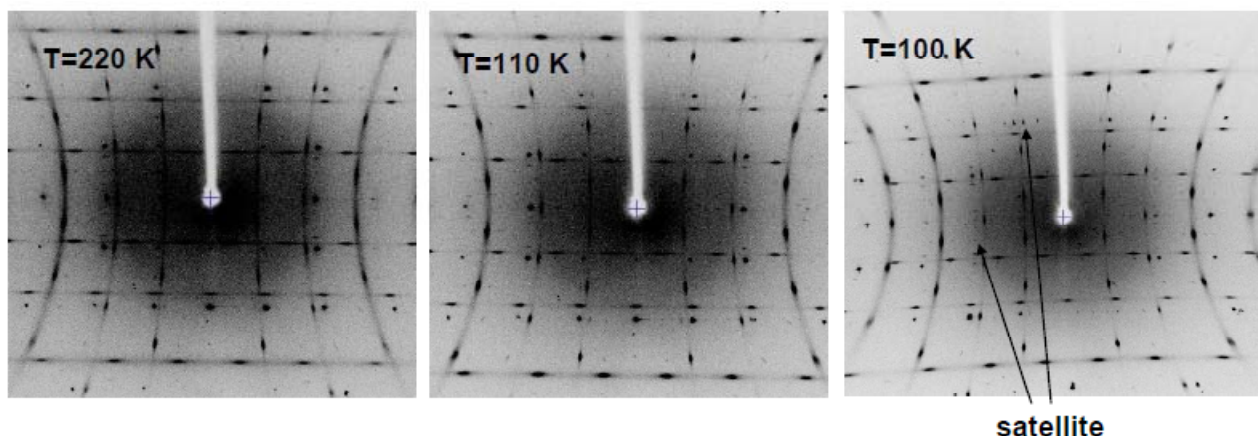


Figure 4. Diffraction images recorded with the X-ray beam parallel to the c^* at different temperatures.

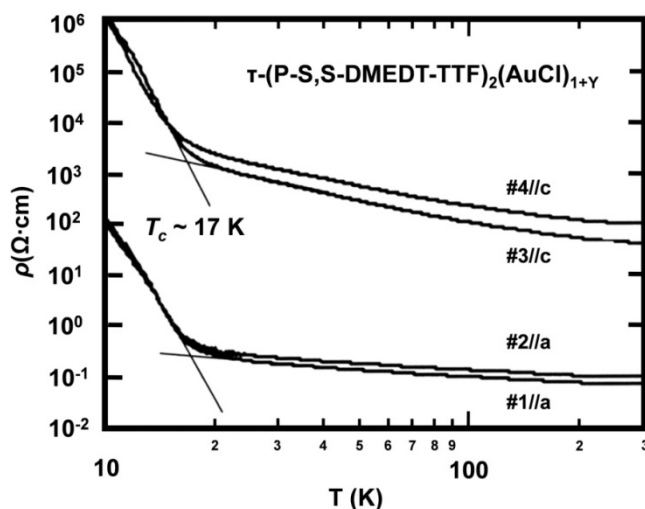
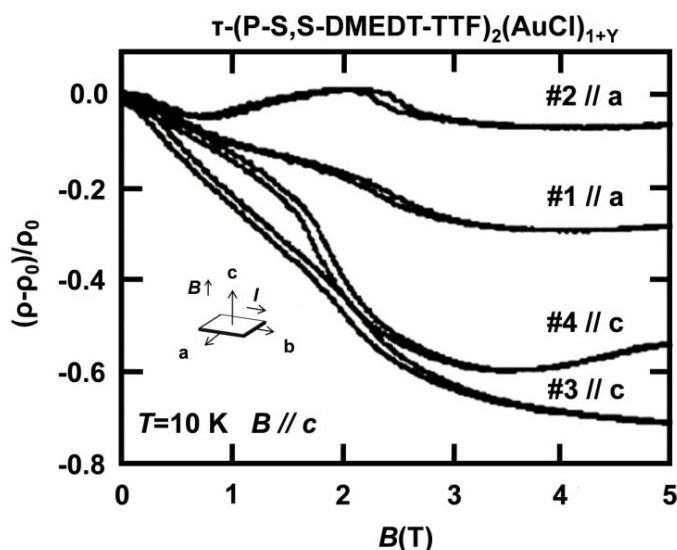


The images show the same features down to 110 K (Figure 4), where satellite peaks start to appear, which are clearly seen at the temperature of 100 K. These satellite peaks are clearly between the Bragg peaks which correspond to the ordered part of the structure (usually the “conducting” layer) and not on the diffusion lines which come from disordered AuCl_2 anions. This observation indicates that the probable origin of these satellites is a modulation of the ordered donor-anion part of the structure. The modulation wavelength is estimated to be approximately $5 \times a^*$ (or $5 \times b^*$). Satellites between Bragg peaks have also been observed in an analogous system [10] and have been interpreted as a transition that couples the anionic layer with the conducting one. Our current measurements are not enough to support a more rigorous interpretation and farther experimental study is needed.

2.2. Electrical Behavior

The results of the electrical measurements reported have been obtained from four crystals (No. 1–4) with the current parallel to a - or to c -axis. It was found that the room temperature values are $\sigma_a = 10.89$, $\sigma_a = 13.87$, $\sigma_c = 0.023$ and $\sigma_c = 0.01 \text{ S cm}^{-1}$, for the crystals 1,2,3 and 4, respectively. This means that the anisotropy σ_a/σ_c is *ca.* 400–1400 at room temperature. Figure 5 shows the temperature dependence of resistivity of three samples. In all cases the crystals exhibit an increase of resistivity with the decreasing of temperature, *i.e.*, a semiconducting behavior, with activation energy of *ca* 18 meV. In all cases the gradients of ρ change at *ca* 17 K. Also, it was found that under a magnetic field of 5 T the resistivity decreases as the temperature decreases.

Figure 6 shows the magnetic field dependence of ρ_a and ρ_c at 10 K. One can see that the magnetoresistance becomes negative by increasing the magnetic field. It is expected to become more negative at lower temperatures as in the cases of similar metallic crystals of τ -phase [3]. The magnetically hysteretic electronic properties at low temperature and a sudden appearance of negative magnetoresistance seem to suggest a close relation of these phenomena to electron correlation and magnetism (See [3,4,6,7]).

Figure 5. Temperature dependence of ρ_a and ρ_c .**Figure 6.** Magnetic field dependence of ρ_a and ρ_c .

3. Experimental Section

Crystals of the compound were prepared by methods reported in [1,3] for AuBr₂-analog using *n*-Bu₄NAuCl₂ instead of *n*-Bu₄NAuBr₂.

A black crystal with dimensions 0.06, 0.5, 0.63 mm glued on a fiber, was used for all data collections. Diffraction measurements were made on a Rigaku R-Axis SPIDER Image Plate diffractometer using graphite monochromated Mo K α or Cu K α radiation. Data collection (ω -scans) and processing (cell refinement, data reduction and Empirical or numerical absorption correction for the Cu K α data) were performed using the CrystalClear program package [14]. The low temperature data were collected using the cryogenic Crystal Cooler System X-stream 2000, Rigaku/MSC. Two data sets were analyzed, one recorded at RT (Mo K α radiation) and the other at 260 K (Cu K α). Important crystallographic data and refinement details for both data sets are listed in Table S1. Further crystallographic information is given as supplementary material (Tables S2–S5 contain atom positions, bond length and bond angles for both data sets and in Figure 1S the numbering scheme of atoms and

the intermolecular contacts are presented). Because of the diffusion streaks recorded on the diffraction images only the Bragg peaks from the ordered part of the structure were integrated and used for structure analysis. The structures were solved by direct methods using SHELXS-97 [15] and refined by full-matrix least-squares techniques on F^2 using SHELXL-97 [16]. Hydrogen atoms were introduced in calculated positions as riding on bonded atoms. All non-H atoms were refined anisotropically.

Resistivity measurements were performed on single on single crystal making contacts with Au paste and Au wires of 10 μm , using the instrumentation reported in [5,6].

4. Conclusions

The compound $\tau\text{-(P-S,S-DMEDT-TTF)}_2(\text{AuCl}_2)$ (AuCl_2) $_y$ shows a q-2D semiconducting behavior from RT to 10 K, a completely different behavior from the 1Br analogue compound which is a quasi 2D conductor at least at low temperatures. For a deeper understanding of this difference further work is underway and especially crystallographic, in order to explain the structural origin of the satellite peaks observed at temperatures below 110 K.

Conflict of Interest

The authors declare no conflict of interest.

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