

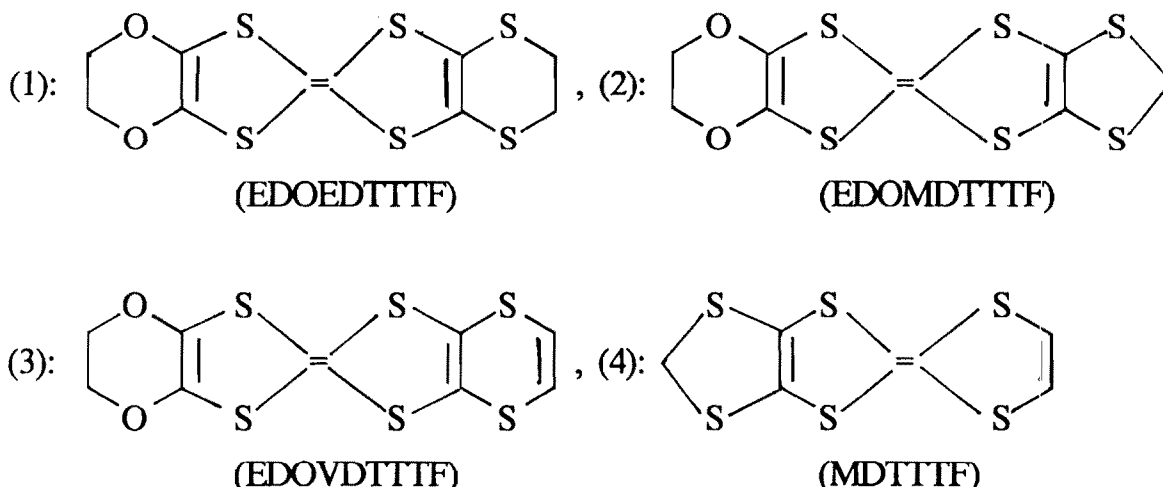
CONDUCTING AND SUPERCONDUCTING CRYSTALS BASED ON SOME UNSYMMETRICAL DONOR MOLECULES

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INTRODUCTION

Recently, a number of conducting and superconducting salts based on unsymmetrical π -donor molecules have been prepared and studied (see [1-5]). In this paper the preparations, crystal structures and physical properties of some salts based on the unsymmetrical π -donors ethylenedioxyethylenedithiotetrathiafulvalene (1), ethylenedioxymethylenedithiotetrathiafulvalene (2), ethylenedioxyvinylenedithiotetrathiafulvalene (3) and methylenedithiotetrathiafulvalene (4) are described.



EXPERIMENTAL

Compounds (1), (2) and (3) were prepared by coupling of 4,5-ethylenedioxy-1,3-dithio-2-one with 4,5-ethylenedithio-1,3-dithiole -2-one, 4,5-methylenedithio-

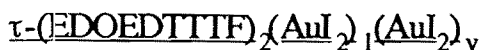
1,3-dithiole-2-one, and 4,5-vinylenedithio-1,3-dithiole-2-one, respectively, via triethyl phosphite at ca 150 °C, followed by column-chromatography separation [3,6]. Compound (4) was prepared by a two-steps sequence: coupling of 4,5-methylenedithio-1,3-dithiole-2-one with 4,5-bis(methylcarboxy)-1,3-dithiole-2-thione, chromatography-separation of the cross-coupling product from the self-coupling products and then demethoxycarboxylation with LiBr in hexamethylphosphoramide, followed by chromatography-separation [1,7]. It was found that the values of half-wave oxidation potentials of (3) are close to those of BEDTTTF, while those of (1), (2) and (4) are lower. This means that substitution of an alkylenedithio-group or vinylenedithio-group by an ethylenedioxy-group increases the donor-capacity of the compound [1]. However, the difference between the second and first oxidation potential of (3), (4) and BEDTTTF is almost the same (see also [8]). The compounds (1)-(4) gave charge transfer complexes with TCNQ. This is a consequence of their low oxidation potentials. Also, a number of cation radical salts was prepared in single crystal form, mainly, by electrochemical crystallization in CH₂Cl₂. β'-(EDOVDTTTF)₂I₃ was prepared by chemical reaction of (3) with Bu₄Ni₃ in CH₂Cl₂ and slow evaporation of the solvent. Data collection for the crystal structure determination was performed on a computer-controlled diffractometer with MoKα Nb-filtered radiation [9]. Electrical conductivity measurements were performed by a four-probe method. Measurements of static susceptibility on a polycrystalline sample of κ-(MDTTTF)₂AuI₂ were performed with a standard Faraday balance between 4 and 290 K in presence of a magnetic field strength of 1.1 T. Magnetization measurements at low temperatures were performed with a SQUID magnetometer working with a variable magnetic field strength. Resonance Raman spectra of the three different phases of (EDOVDTTTF)_xI₃ were recorded at room temperature with a Jobin Yvon Ramanor Laser Raman spectrophotometer, using for excitation the 488 nm line.

RESULTS AND DISCUSSION

From a large number of conducting salts prepared from the donors (1)-(4) only eleven of them, which crystallized well in single crystal form, were studied. Most of the crystals obtained from (1), (2) and (3) crystallize in tetragonal system, which is rarely observed in organic conductors. They have the formula D_x(X)₁(X)_y, where D=donor and X=anion. In this case a new kind of side-by-side arrangement of the donor molecules was observed.



It crystallizes as thin dark-brown plates [10]. It is metallic ($\sigma_{\text{RT}}=29$ S/cm, MIT at ca25K). Details on the temperature dependence of the conductivity are given in Fig.1a.



It crystallizes as black big crystals, in the tetragonal system, space group P42c, a=7.485 c=34.032 Å, Z=4. It is semiconducting ($\sigma_{\text{RT}}=4.6 \times 10^{-5}$ S/cm).



It crystallizes as black plates in the orthorhombic system, space group A222,

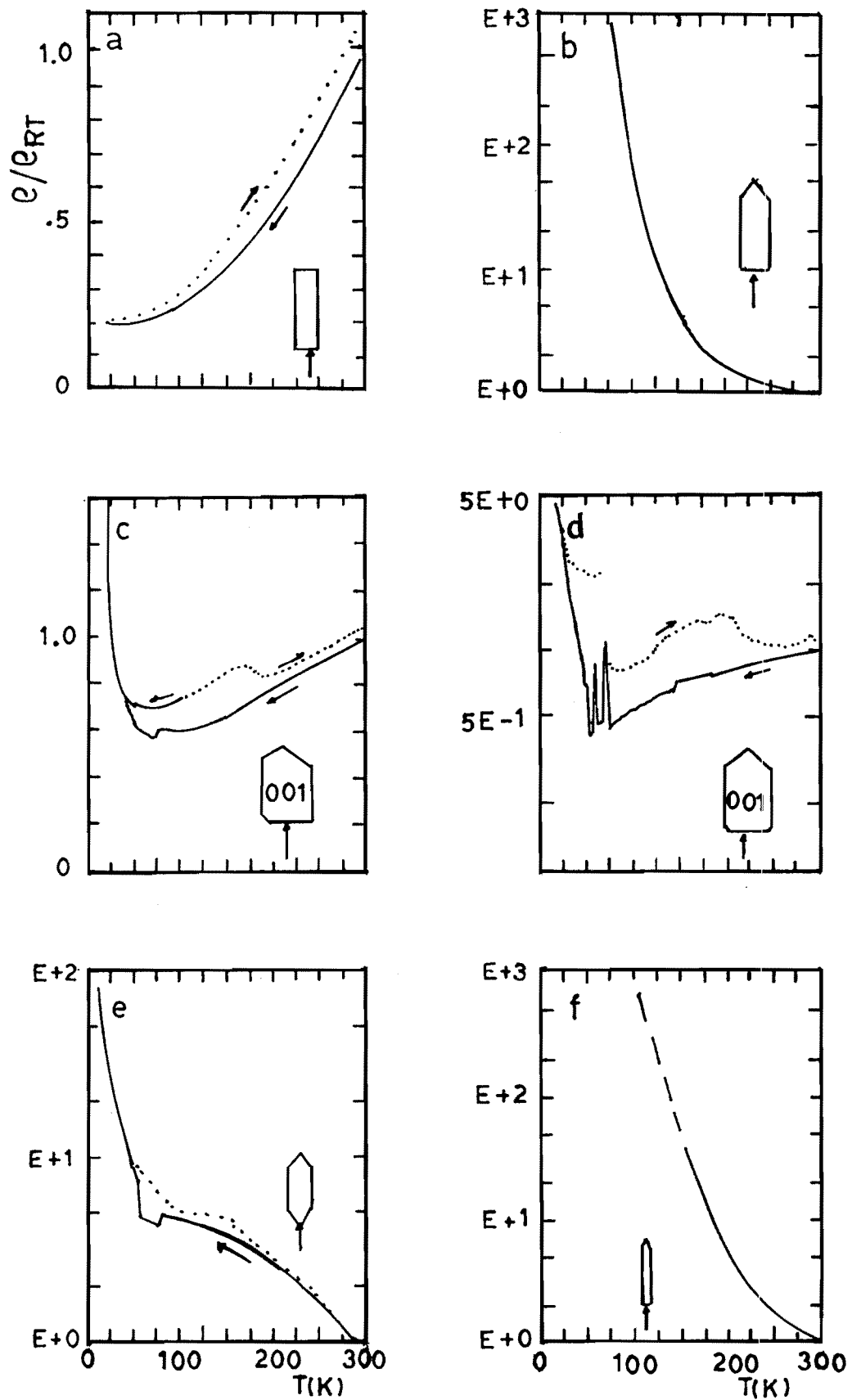


Fig.1. Temperature dependence of the normalized resistivity of $(\text{EDOEDTTTF})_2\text{Cu}(\text{NCS})_2$ (a), τ - $(\text{EDOMDTTTF})_2(\text{I})_1(\text{I})_y$, τ - $(\text{EDOVDTTTF})_2(\text{AuI})_1(\text{AuI})_y$ (c), τ - $(\text{EDOVDTTTF})_2(\text{IBr})_1(\text{IBr})_y$ (d), $(\text{EDOVDTTTF})_x\text{AuBr}_2$ (e), and β' - $(\text{EDOVDTTTF})_2\text{I}_3$ (f) measured along the arrow-direction, in the temperature range from 15 to 300 K.

$a=6.621, b=7.248, c=33.239 \text{ \AA}, Z=2$. It is semiconducting ($\sigma_{RT}=4 \times 10^{-3} \text{ S/cm}$).



It crystallizes as black plates in the tetragonal system, space group P42c. It is semiconducting ($\sigma_{RT}=0.2 \text{ S/cm}$). Details on the temperature dependence of the conductivity are given in Fig.1b.



It crystallizes as black plates in the tetragonal system, space group P42c, $a=7.471, c=33.584 \text{ \AA}, Z=4$. It is metallic ($\sigma_{RT}=180 \text{ S/cm}$, MIT at ca 60K). Details on the temperatures dependence of the conductivity are given in Fig.1c.



It crystallizes as black plates in the tetragonal system, space group P42c. It is metallic ($\sigma_{RT}=60 \text{ S/cm}$, MIT at ca 70K). Details on the temperatures dependence of the conductivity are given in Fig.1d.



It crystallizes as black plates. It is semiconducting ($\sigma_{RT}=11\text{-}22 \text{ S/cm}$). Details on the temperature dependence of the conductivity are given in Fig.1e.



It crystallizes as black needles in the monoclinic system, space group P2₁. It is semiconducting. Resonance Raman spectra showed bands at 108, 217, 330 cm^{-1} .



It crystallizes as bronze needles. It is semiconducting ($\sigma_{RT}=10.4 \text{ S/cm}$). Details on the temperature dependence of the conductivity are given in Fig.1f. Resonance Raman spectra showed bands at 107, 214, 329 cm^{-1} .



It crystallizes as black plates with a golden lustre in the tetragonal system, space group P42c, $a=7.563, c=33.883 \text{ \AA}, Z=4$. A stereoview of the crystal structure is shown in Fig.2. There is no stacking of the donor-molecules. The large axis of the donor-molecules is parallel to the c-axis. The donor-molecules form extended layers parallel to the a- and b- axes at $a=b=0.5$. There is one I_3 , which is well behaved, at the origin. The rest of I_3 is disordered. The whole y-axis at $x=0.5$ and $z=0.25$ is full of electronic density [10]. There is a disorder of the ethylenedioxy-group, as well, there are intermolecular (S---O)-contacts ($\geq 3.50 \text{ \AA}$) between the S and O atoms of vinylene-and ethylene-group, respectively, and (S---S)-contacts ($\geq 3.58 \text{ \AA}$) between the sulfur atoms of TTF-cores, forming a 2-dimensional network perpendicular to the c-axis. The compound is metallic. The temperature dependence of the conductivity varies from crystal to crystal. Fig. 3 shows the temperature dependence of the conductivity for one crystal with $\sigma_{RT}=45 \text{ S/cm}$. One

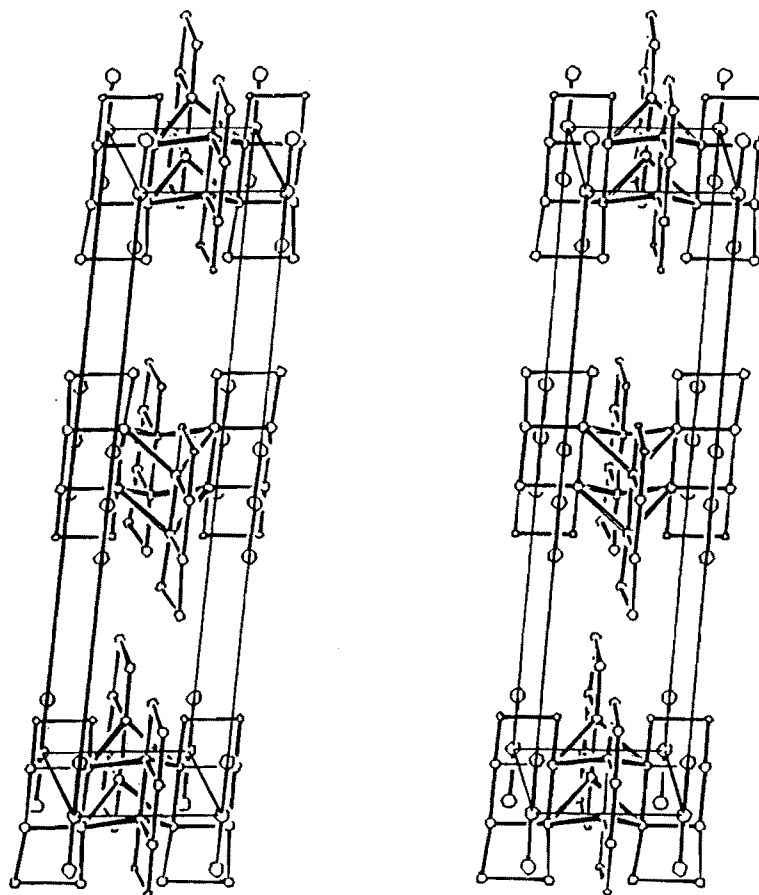


Fig.2. Stereoview of the molecular packing of τ -(EDOVDTTTF)₂(I₃)₁(I₃)_y. The disordered I₃ is not shown.

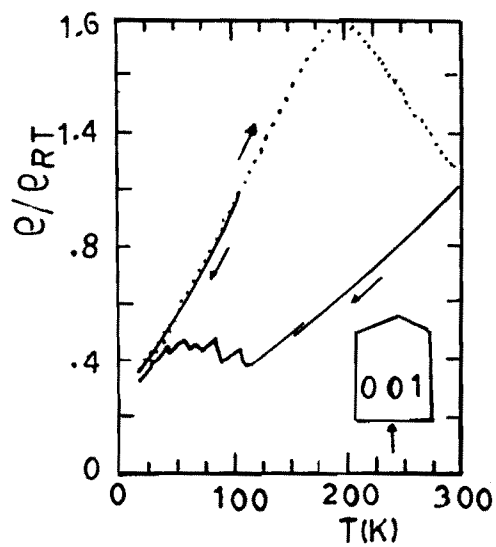


Fig.3. Same as in Fig.1, but for one crystal of τ -(EDOVDTTTF)₂(I₃)₁(I₃)_y

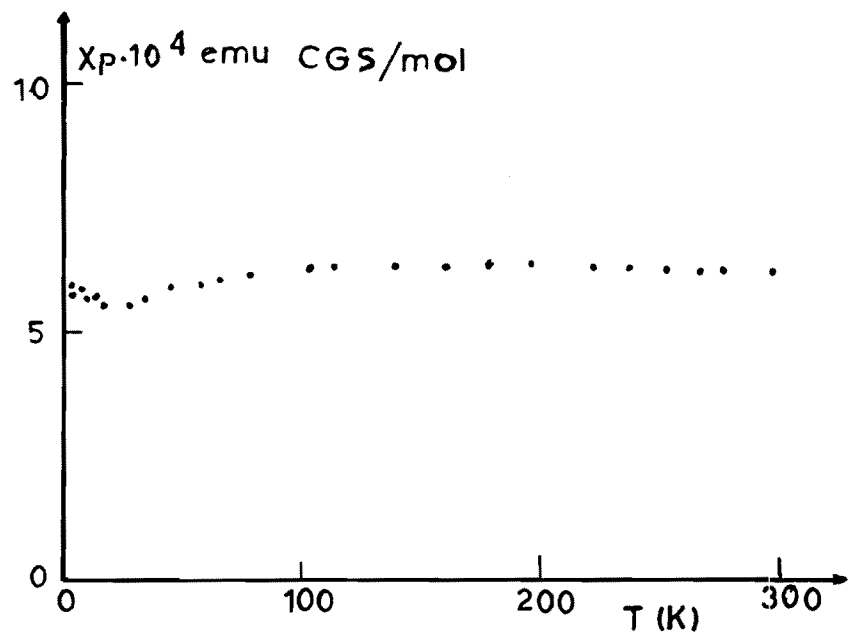


Fig.4. Temperature dependence of paramagnetic susceptibility of a polycrystalline sample of $(\text{MDTTTF})_2\text{AuI}_2$ in the temperature range from 4K to 290 K.

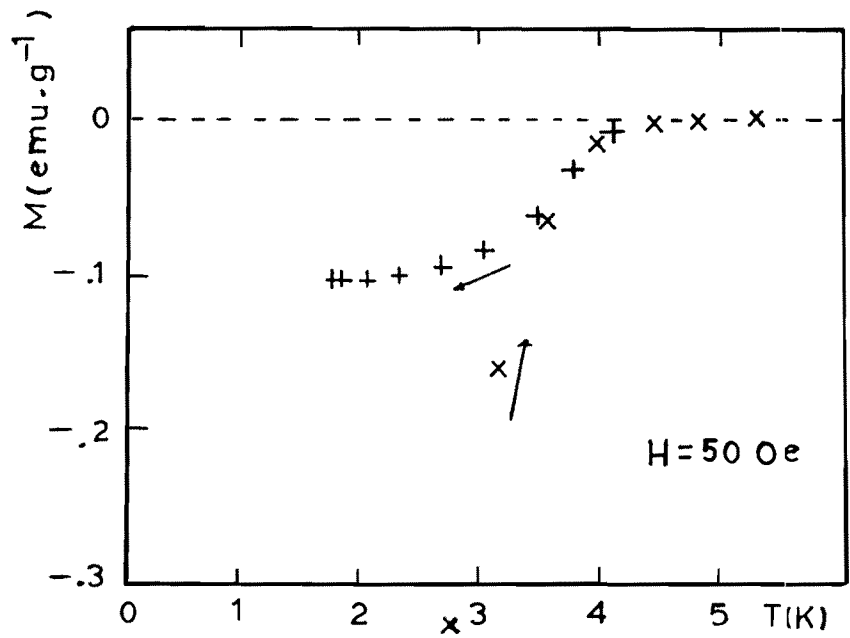


Fig.5. Temperature dependence of magnetization of $(\text{MDTTTF})_2\text{AuI}_2$ at low temperatures (1.8-5K).

can see that on cooling down sudden drops in the conductivity began occurring around 150K. They disappeared after heating from 25K to 120 K and recooling to low temperatures. There is a 2-dimensional metallic conductivity, which is due to S---S interactions parallel to ab-plane. These preliminary results indicate that the crystal could remain metallic or become superconducting at very low temperatures. Resonance Raman spectrum showed bands at 108, 135(sh), 215-250(br), 335-345(br) cm^{-1} . The shoulder at 135 cm^{-1} indicates the disorder of I_3 . Weissenberg photographs and Raman spectra showed that the disorder of I_3 decreases after heating the crystals at ca 70°C for three days. Perhaps, the observed metallic properties result from the presence of anion vacancies producing slightly nonstoichiometric crystals as in the case of $\zeta\text{-(ET)}_2(\text{I}_3)(\text{I}_5)$ [11].

$\kappa\text{-(MDTTF)}_2\text{AuI}_2$

It crystallizes as black-brown plates in the orthorhombic system, space group Pbcm [9]. It is metallic ($\sigma_{\text{RT}}=12\text{-}36$ S/cm) and becomes superconducting at low temperature ($T_c=5\text{K}$) [4,12-14]. The temperature dependence of the paramagnetic susceptibility of a polycrystalline sample is shown in Fig.4. It indicates a Pauli paramagnetism. The temperature dependence of magnetization at lower temperatures (1.8-5K) is shown in Fig.5. For the observation of the diamagnetic shielding and Meissner effect the sample was first cooled in absence of any magnetic field down to 1.8K, then the field was applied and magnetization was measured upon heating and then it was cooled under magnetic field [15]. The Meissner phase starts to appear at ca 4.3 K (see also [12]), while from conductivity measurements it was found that $T_c=5\text{K}$ [4,13]. Similar results have been obtained from other organic superconductors [16].

Conductivity measurements at lower temperatures under ambient and high pressure as well as magnetic properties of salts based on (1), (2), (3) and similar donors will be published in a future paper.

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