

## RADICAL CATION SALTS OF BEDT-TTF AND AN UNSYMMETRICAL BEDT-TTF DERIVATIVE

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Investigations of several BEDT-TTF and DIMET radical salts are presented. Measurements on  $\beta$ -(BEDT-TTF)<sub>2</sub>IAuI crystals show that their conducting and superconducting properties might vary strongly depending on the decomposition of (IAuI)<sup>-</sup> anions during the electrochemical process.

### 1. INTRODUCTION

BEDT-TTF<sup>S</sup> is at this time the promising donor to prepare new highly conducting organic metals or even superconductors. In the future unsymmetrical substituted donors of the TTF-family might become of similar interest. We report here the preparation and physical investigations on radical cation salts of BEDT-TTF as well as on an unsymmetrical BEDT-TTF derivative DIMET<sup>SS</sup>.

### 2. RESULTS AND DISCUSSION

#### 2.1. $\beta$ -(BEDT-TTF)<sub>2</sub>IAuI

Since the discovery of superconductivity in the organic metal  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> (1) at ambient pressure<sup>1-3</sup> effort has been made in different laboratories<sup>4-9</sup> in the preparation of other trihalide salts of BEDT-TTF. Besides the crystals of 1 the isostructural  $\beta$ -(BEDT-TTF)<sub>2</sub>IAuI (2)<sup>6,8,9</sup> is of substantial interest because of the high  $T_C \approx 4K$  for the superconducting transition at ambient pressure without any special pressure cycle as for the ambient pressure  $T_C = 8K$  superconducting state for crystals of 1<sup>10</sup>. Nevertheless, in contrast to electrocrystallization of 1 in the case of 2 exists a problem due to the fact that during the electrochemical process the

anion (IAuI)<sup>-</sup> is decomposed. This can be deduced from the gold deposition on both platinum electrodes whereby the thickness of the gold layer depends strongly on the time of the electrocrystallization process. Therefore it has to be assumed that during the electrochemical crystallization also "impurities" like iodide, iodine and I<sub>3</sub><sup>-</sup> anions are present and that their concentration increases with time. These "impurities" can partly replace (IAuI)<sup>-</sup> anions in the lattice. This has the consequence that depending on their concentrations in different crystals the following observations are made: a) The onset temperature for superconductivity varies over a broad temperature range (3-5K); b) the superconducting transition might become very broad or in the worst case is even suppressed; c) the critical currents and magnetic fields vary strongly; d) quite different ratios between the room temperature value of the resistivity and the low temperature (5K) value  $\rho_{300}/\rho_5$  are obtained and become small for impure crystals.

Taking into account these facts the best crystals with respect to the superconducting properties should be obtained from electrocrystallizations as short as possible. This implies experi-

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<sup>S</sup>BEDT-TTF= Bis(1,2-ethylenedithiolo)-tetrathiafulvalene

<sup>SS</sup>DIMET = 4.5-Dimethyl-4'.5'-ethylenedithiolo-tetrathiafulvalene

ments on small crystals. In fact, Carlson et al.<sup>9</sup> found the highest onset temperature of 4.98K for the smallest crystal they used in their experiments. In order to investigate the above facts, we have measured several larger crystals ( $3 \times 1 \times 0.3 \text{ mm}^3$ ) which were grown during about 14 days by electrochemical oxidation of BEDT-TTF at 21°C in the presence of  $n\text{-Bu}_4\text{-NAuI}_2$  as the supporting electrolyte. Dry tetrahydrofuran was used as a solvent (see also ref. 11).

In figures 1-6 typical results for such crystals are presented. Fig. 1 shows the resistivity along the a-direction of two such crystals of 2 in the temperature range between 5 and 300K. The measurements were done on crystals of about 3 mm length with the standard four probe method. The ratios  $\rho_{300}/\rho_5$  are about 25 for sample I resp. 160 for sample II indicating strong variations. Both values are small with respect to the typical value of about 500 - 1000 for the isostructural crystals of 1.

Typical data for the temperature dependence of the thermopower of 2, measured along the a-direction are given in fig. 2. The room temperature value is the same as for crystals of 1<sup>12</sup>, but in contrast to this earlier result where in the whole temperature range for this direction the thermopower was positive, here the thermopower changes from positive to negative values at about 210 K and quite large negative values are observed. The thermopower data in fig. 2 are very similar to those measurements of Mortensen et al.<sup>13</sup> for their crystals of 1. We explain the difference in the thermopower data reported here compared to our earlier measurements on crystals of 1 with the "impurities" in 2. By using a two-dimensional tight binding model for the linear temperature dependent part we get here a much smaller conduction band width ( $\sim 0.1 \text{ eV}$ ) for 2 as we obtained for 1 ( $\sim 0.26 \text{ eV}$ ). In our opinion this result is not consistent with the fact that these two compounds are isostructural.

Fig. 3 shows the low temperature part of the resistivity of another crystal of 2 ( $\rho_{300}/\rho_5 \sim 250$ ) which was measured by the Montgomery method along the a- and b-directions. At room temperature the ratio  $\rho_a/\rho_b = 3.3$  while at 10 K this value is 5.0 (for crystals of 1 we found a more or less constant value of 3.3 over the whole temperature range). At 4K the resistivity decreases strongly in both directions leading to zero resistivity at 3K, indicating a total superconducting transition.

In contrast rf penetration depth-measurements show that the superconducting transition is much broader. Fig. 4 shows the increase in resonance frequency of a LC-circuit (3 MHz) due to exclusion of the rf-field by diamagnetic shielding currents in the sample (a-c susceptibility) by lowering the temperature. The onset of superconductivity - in a similar size crystal as used for the conductivity measurements - lies around 4K but the transition is very broad. The signal, which still increases on cooling at 1.3K is about 40 % of that expected for a perfect superconductor and indicates an inhomogeneous  $T_c$ -distribution in the sample.

Fig. 5 shows the temperature dependence of the upper critical fields  $H_{c2}$  for magnetic fields parallel and perpendicular to  $c^*$ . The investigations were done on sample II of fig. 1 by measuring the resistivity (current flow along a-direction). Additionally, the measurements (---) obtained by Carlson et al.<sup>9</sup> by rf-penetration depth measurements are drawn. The critical fields we obtained by resistivity measurements are much smaller with respect to the values of ref. 9 (at 1.3K: 0.38T for the magnetic field parallel to  $c^*$  and 3.2T for the field perpendicular to  $c^*$ ).

Fig. 6 demonstrates the magnetoresistance of the same sample as in fig. 5 (in the same directions) at 4.2K. Very similar curves were obtained at 1.3K with the only difference that at this temperature the superconducting transition

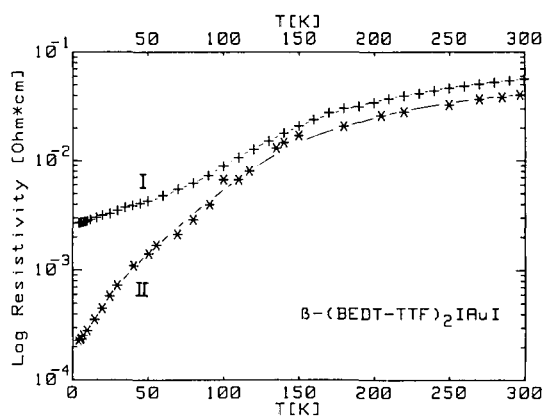


FIGURE 1 Resistivity in a-direction of two crystals (I, II) of  $\beta$ -(BEDT-TTF)<sub>2</sub>IAuI

was observed. The magnitude of the magnetoresistance  $M(B) = \langle R(B) - R(0) \rangle / R(0)$  with a magnetic field of  $B = 7.5$  T along the  $c^*$ -axis is about 5% (error  $\pm 1\%$ ) and perpendicular to the  $c^*$ -axis about 2% (current flow along the a-direction). Similar values were observed for crystals of 1 and  $\beta$ -(BEDT-TTF)<sub>2</sub>IBr<sub>2</sub><sup>5</sup>. A second sample of 2 with a resistivity ratio  $\rho_{300}/\rho_5 \approx 90$  gave smaller magneto-resistance values at 7.5 T of about 3% resp. 1%. This indicates that the magneto-resistance at low temperature can be described in terms of a relaxation time ( $\tau$ ) approximation based on a two-dimensional band picture. In this

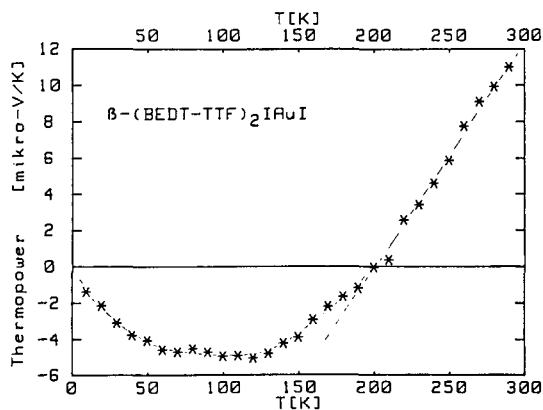


FIGURE 2 Thermopower of  $\beta$ -(BEDT-TTF)<sub>2</sub>IAuI in a-direction

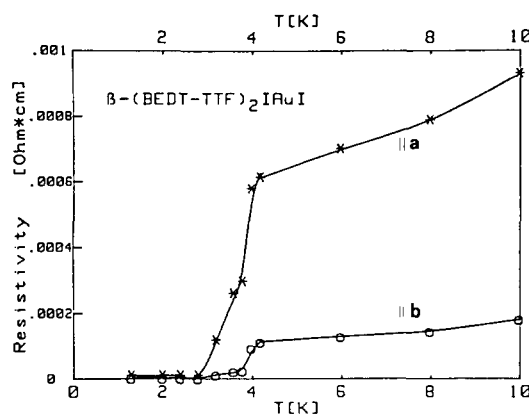


FIGURE 3 Resistivity of  $\beta$ -(BEDT-TTF)<sub>2</sub>IAuI below 10K parallel to the a- and b-directions

approximation  $(M(B))^{1/2} = \omega_c \tau = eB\tau/m_c^*c$  with  $\omega_c$  the cyclotron frequency and  $m_c^* = \sqrt{m_x m_y}$  the cyclotron effective mass. This result for 2 is in contrast to the case of (TMTSF)<sub>2</sub>ClO<sub>4</sub>.

The above reported results indicate that in crystals of  $\beta$ -(BEDT-TTF)<sub>2</sub>IAuI "impurities" like  $I^-$ ,  $I_2$  and  $I_3^-$  affect strongly the superconducting properties.

### 2.2. BEDT-TTF nitrates

The preparation and physical properties of  $\alpha$ -(BEDT-TTF)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub> (3) was reported recently by us<sup>14</sup>. By varying the concentration of the electrolyte salt tetrabutylammoniumnitrate in the THF-solution as well as the dynamic conditions of the electrochemical cell three further phases could be obtained separately. While the crystals

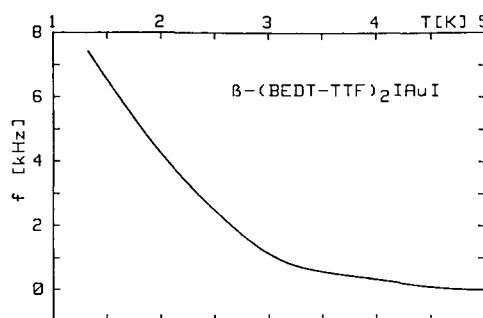


FIGURE 4 Ac-susceptibility of  $\beta$ -(BEDT-TTF)<sub>2</sub>IAuI (see text)

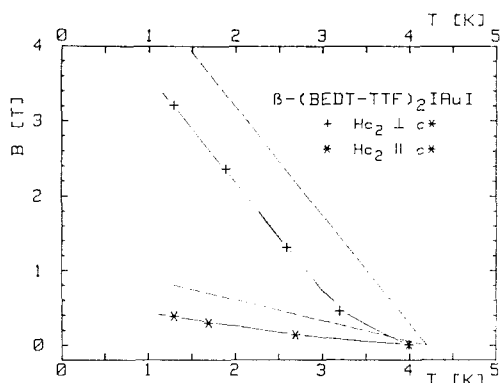


FIGURE 5  
Critical fields  $H_{c2}$  of  $\beta$ -(BEDT-TTF) $_2$ IAuI

of 3 have a long (up to 2 cm) plate-like shape and are metallic down to about 30K<sup>14</sup>, crystals of  $\beta$ -(BEDT-TTF) $_3$ (NO $_3$ ) $_2$  (4) and  $\gamma$ -(BEDT-TTF) $_2$ NO $_3$  (5) form needles resp. cubes and both phases are semiconductors with room temperature conductivities  $\sigma_{300} \sim 10^{-3} (\Omega\text{cm})^{-1}$  for 4 and  $\sim 10^{-1} (\Omega\text{cm})^{-1}$  for 5. The fourth phase  $\delta$ -(BEDT-TTF) $_x$ (NO $_3$ ) $_y$  consists of thin plates which are metallic at room temperature, but no structure could be obtained yet. For the  $\beta$ - and  $\gamma$ -phases 4 and 5 the following crystallographic data were obtained: 4 = monoclinic  $P2_1/c$ ,  $a=6.529(1)$ ,  $b=12.379(4)$ ,  $c=28.487(11)$ Å,  $\beta=95.01(3)^\circ$ ,  $V=2293.6$  Å $^3$ ,  $Z=2$ ; 5 = monoclinic  $P2_1/n$ ,  $a=30.869(32)$ ,  $b=6.587(4)$ ,  $c=15.026(13)$ Å,  $\beta=101.58(8)^\circ$ ,  $V=2993$  Å $^3$ ,  $Z=4$ .

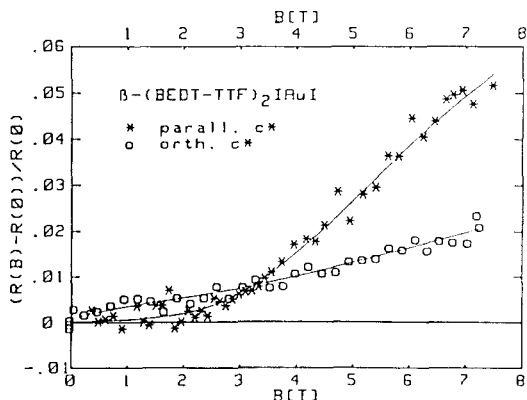


FIGURE 6  
Magnetoresistance of  $\beta$ -(BEDT-TTF) $_2$ IAuI

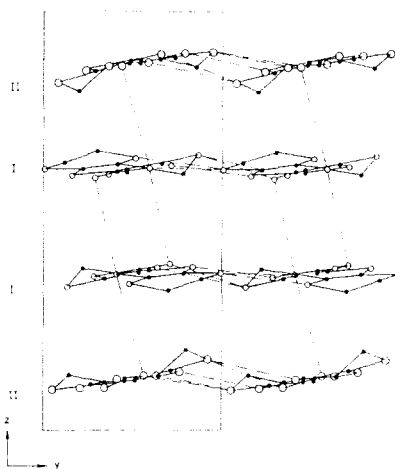


FIGURE 7  
Projection of the unit cell of  $\gamma$ -(BEDT-TTF) $_2$ NO $_3$  parallel to the a-direction (see text)

In both phases 4 and 5 the donor stacks are aligned in sheets and the most important S...S contacts are between adjacent stacks. As an example fig. 7 shows a section of the donor sheets of the  $\gamma$ -phase projected parallel to the a-direction. Intermolecular S...S contacts  $< 3.8$  Å are indicated by broken lines. Both phases 4 and 5 have different overlap-patterns whereby one overlap is remarkable because the long molecular axes are not parallel. Therefore both phases 4 and 5 have semiconducting properties.

The fact that up to now four different nitrate phases of BEDT-TTF could be obtained demonstrates again that many molecular arrangements of this donor in the crystal lattice are possible.

### 2.3. DIMET radical cation salts

An even larger variety of molecular arrangements seems to appear in crystals of the unsymmetrical donor DIMET<sup>15,16</sup>. This new donor was electrocrystallized in different solvents using tetrabutylammonium-salts of various anions like ClO $_4^-$ , ReO $_4^-$ , NO $_3^-$ , I $_3^-$ , (IAuI), PF $_6^-$ , AsF $_6^-$  and SbF $_6^-$  as electrolytes. With all anions radical salts were obtained and several of them showed metallic properties at room temperature<sup>15</sup>. The only problem

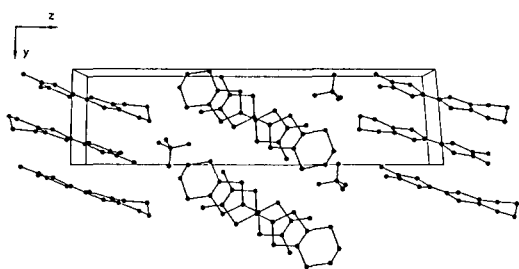


FIGURE 8

Projection of the unit cell of  $(\text{DIMET})_2\text{ClO}_4$  along the  $a$ -direction

in the electrocrystallization is that solvent molecules are easily incorporated on fixed positions into the crystals. In order to prevent this incorporation of solvent molecules we prepared radical salts from a solvent which does not fit into the lattices (trichlorethane) and obtained a new type of structure. Instead of the radical salt  $(\text{DIMET})_2\text{ClO}_4 \cdot x\text{THF}$  we obtained now crystals of  $(\text{DIMET})_2\text{ClO}_4$  (**6**). The crystals of **6** have the following data: triclinic  $P\bar{1}$ ,  $a=7.000(2)$ ,  $b=7.824(3)$ ,  $c=27.010(14)\text{Å}$ ,  $\alpha=88.10(4)$ ,  $\beta=89.02(4)$ ,  $\gamma=74.58(3)^\circ$ ,  $V=1425\text{Å}^3$  and  $Z=2$ . As a very unusual feature in organic radical salts two donor species are arranged to crystallographically inequivalent stacks running parallel to  $a$  and  $b$  as can be seen from a projection along  $a$  in fig. 8. The stacks are arranged side by side perpendicularly to the long molecular axes forming sheet-like arrangements. Due to short interstack S...S contacts this leads to a more or less two-dimensional character within each sheet. Due to the more or less perpendicular arrangement of the sheets the crystals show a three-dimensional conducting behaviour. Further crystallographic details<sup>17</sup> as well as physical properties will be reported separately.

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