TWO POLYMORPHIC MODIFICATIONS OF (BEDT-TTF)$_2$ICl$_2$ CRYSTALS
WITH METALLIC AND SEMICONDUCTOR PROPERTIES

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Discovery of superconductivity at normal pressure in the $\beta$ phase of bis(ethylenedithio)tetrathiafulvalene triiodide $\beta$-(BEDT-TTF)$_2$I$_3$ [1] has stimulated work on the synthesis of BEDT-TTF radical-cation salts, which has led to preparation of new superconducting salts (isostructural to the triiodide) of BEDT-TTF with IBr$_2^-$ and AuI$_2^-$, which are close to I$_3$ in size [2-4]. With the goal of further study of the effect of the size of the linear anion on the structure and electrical conduction properties of polyhalides of BEDT-TTF, we have synthesized the salts of BEDT-TTF with the ICl$_2^-$ anion. On two of the obtained polymorphic modifications of composition (BEDT-TTF)$_2$ICl$_2$, we have observed substantially different properties: one of them (the $\beta$ phase) is a metal, the other (the $\beta'$ phase) is a semiconductor.

EXPERIMENTAL

Purification of the Solvents and the Starting Materials. BEDT-TTF was successively recrystallized from pyridine and chlorobenzene. Et$_4$NICl$_2$ was obtained using the technique in [5] and crystallized twice from ethanol and dried under vacuum. Benzonitrile was dried over molecular sieves and distilled under vacuum above P$_2$O$_5$. The THF was purified by successive distillations under an inert atmosphere above KOH and CaH$_2$. Immediately before use, the THF was passed through a column filled with basic aluminum oxide of first degree of activity.

Synthesis of $\beta$-(BEDT-TTF)$_2$ICl$_2$ and $\beta'$-(BEDT-TTF)$_2$ICl$_2$. a) To a hot (\~90$^\circ$C) solution of 0.06 g (1.56.10$^{-4}$ mole) BEDT-TTF in 45 ml benzonitrile, we added under Ar a hot solution of 0.107 g (3.12.10$^{-4}$ mole) Et$_4$NICl$_2$ in 15 ml benzonitrile. The reaction mixture was cooled down to 20$^\circ$C at a rate of 1.5$^\circ$C/h and then held at this temperature for 7 days. The precipitated crystals, black needles ($\beta'$ phase) and dark-brown plates ($\beta$ phase), were filtered, washed with benzonitrile and acetone, and dried under vacuum.

b) 0.0156 g (4.10$^{-5}$ mole) BEDT-TTF and 0.0328 g (1.0.10$^{-4}$ mole) Et$_4$NICl$_2$ were dissolved with mixing under Ar in 20 ml THF. They were dissolved directly in an H-shaped electrochemical cell separated by a glass porous membrane. After dissolution, the liquid levels were equalized in both arms of the cell and platinum electrodes were inserted into them (wire of diameter 1 mm, sealed in glass). The working electrode (the anode) was prepolarized in 1 M H$_2$SO$_4$, first anodically, then cathodically. The electrodes were washed with twice-distilled water and dried in a furnace under a stream of nitrogen. The cell was thermostated (25$^\circ$C) and connected to a battery fitted with a dc stabilizer. The electrowallization was carried out for 3 days at $i = 1.5$ $\mu$A and current density 5 $\mu$A/cm$^2$. The crystals of the salt ($\beta'$ phase) were grown on the anode (needles of length up to 3 mm); they were filtered, washed with THF and acetone, and dried under vacuum. When we increased the electrolyte concentration by a factor of 5, crystals of $\beta$ phase were formed along with the $\beta'$ phase.

X-ray Diffraction Analysis. The basic crystallographic data for the crystals of $\beta$- and $\beta'$-(BEDT-TTF)$_2$ICl$_2$ are presented in Table 1. The experimental set of intensities for the $\beta'$ crystals* (3170 independent reflections with $I > 2\sigma$) were obtained on the Syntex P1 diffractometer in MoK$_\alpha$ radiation with graphite monochromator in the region up to (sin $\theta$\lambda)$_{\text{max}} = 0.808$.

*For the $\beta$ crystals, the x-ray experiment is described in [6].
TABLE 1. Crystallographic Data for the $\beta$ and $\beta'$ Phases of (BEDT-TTF)$_2$ICI

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$\beta'$</th>
<th>$\beta$</th>
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<tbody>
<tr>
<td>$a$, Å</td>
<td>6.638(1)</td>
<td>5.734(3)</td>
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<tr>
<td>$b$, Å</td>
<td>9.760(2)</td>
<td>8.979(7)</td>
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<td>$c$, Å</td>
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<td>$\alpha$, deg</td>
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<td>$\beta$, deg</td>
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<td>$\gamma$, deg</td>
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<tr>
<td>$V$, Å$^3$</td>
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<td>806.2(1,3)</td>
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<tr>
<td>Space group</td>
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<td>$d_{calc}$, g/cm$^3$</td>
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TABLE 2

<table>
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<td>C'</td>
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<td>296(3)</td>
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We did not correct for absorption, $\mu(\text{MoK}_\alpha) = 21.8$ cm$^{-1}$. The crystal had dimensions $0.42 \times 0.15 \times 0.08$ mm$^3$.

The structure was deciphered by the heavy-atom method and refined by the least-squares method in the anisotropic approximation (for the H atoms, in the isotropic approximation) to $R = 0.029$. The coordinates of the nonhydrogen atoms are presented in Table 2 (their temperature parameters and coordinates of the H atoms can be obtained from the authors).

Physical Measurements. The conductivity was measured by the four-contact compensation method. The crystal under study, of dimensions $(1-2) \times 0.1 \times 0.05$ mm$^3$, was attached, using a highly conductive graphite paste, to four pre-annealed platinum electrodes of diameter 10 μm. The temperature measurements were made in a glass cryostat with liquid helium in the interval 1.3-300 K.

The thermal emf was measured in the single crystals using the standard technique. The temperature gradient in the sample was not more than 0.5 K.

The magnetic susceptibility was measured by the Faraday method in the temperature interval 1.3-300 K in a magnetic field from 2.8 to 9.0 kOe. The diamagnetic component of the susceptibility, determined from the Pascal rule, was $4.71 \times 10^{-5}$ cm$^3$·mole$^{-1}$ (calculated per formula unit of (BEDT-TTF)$_2$ICl$_2$).

DISCUSSION

Upon oxidation of BEDT-TTF by tetraethylammonium dichloroiodate in a benzonitrile solution, two types of crystals are formed: black needles and dark-brown plates. Complete deciphering of the structure has shown that they are polymorphic modifications ($\beta'$ and $\beta$ respectively) of the radical-cation salt of composition (BEDT-TTF)$_2$ICI$_2$. These same phases are also formed in electrochemical oxidation of BEDT-TTF in a THF solution in the presence of electrolyte Et$_4$NCl$_2$. 1816