Effect of electrocrystallization medium on quality, structural features, and conducting properties of single crystals of the (BEDT-TTF)$_4$A'[Fe$^{III}$]$\text{C}_2\text{O}_4$]$\times$G family†

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A modified procedure for the electrocrystallization of organic conductors with paramagnetic anions of the (BEDT-TTF)$_4$A'[M$^{III}$]$\text{C}_2\text{O}_4$]$\times$G family has been proposed. It is found that single crystals of different phases of the family can be prepared if the electrocrystallization medium is represented by the mixture of 1,2,4-trichlorobenzene (or 1,3-dibromobenzene), 96% ethanol and different solvents (G), only the latter being included into the composition of the resulting salts as neutral guest molecules (G = benzonitrile, fluorobenzene, chlorobenzene, 1,2-dichlorobenzene, bromobenzene, nitrobenzene). Using this approach, a number of known and new BEDT-TTF salts with the tris(oxalato)ferrate anion have been synthesized. Among them, there are superconducting crystals of monoclinic $\beta'$-series with different guest solvents (G) and their mixtures. For the first time, crystals of a triclinic phase (G = 1,2-dibromobenzene), with alternating $\alpha$- and $\beta'$-BEDT-TTF layers and metallic behaviour down to 1.5 K, were obtained. Additionally, monoclinic crystals having another stoichiometry and $\alpha$-type donor packing were prepared.

Introduction

The family of conducting molecular charge transfer salts based on bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) with paramagnetic tris(oxalato)metallate anions, (BEDT-TTF)$_4$A'[M$^{III}$]$\text{C}_2\text{O}_4$]$\times$G, where A' is NH$_4$\textsuperscript{+}, K\textsuperscript{+}, H$_3$O\textsuperscript{+} or Rb\textsuperscript{+}, M$^{III}$ is Fe or Cr and G is a guest solvent molecule, has been intensely investigated over the past years. Since the discovery of the first superconductor in the family (M$^{III}$ is Fe; A' is H$_3$O\textsuperscript{+}; G is PhCN)\textsuperscript{a} six more superconductors and a lot of metals and semiconductor, resulting from variations of A, M and G components, have been synthesized.\textsuperscript{2–16}

In the crystal structure, conducting layers formed by BEDT-TTF radical cations alternate with complex anion layers comprised of [M$^{III}$]$\text{C}_2\text{O}_4$]$\times$- A' + and G. The anion layer has a planar honeycomb arrangement. M$^{III}$ and A' cations linked by oxalate bridges alternate in vertices of a slightly distorted hexagonal network. Neutral solvent (G) molecules occupy hexagonal cavities of the layer and stabilize the structure. The crystals contain a racemic mixture of right ($\Delta$) and left ($\Lambda$) isomers of the chiral [M$^{III}$]$\text{C}_2\text{O}_4$]$\times$ anions. Nevertheless, their distribution in the anion layers can be different, resulting in differences in the conducting layer packing and the transport properties of the crystals.

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Now three series of compounds comprising [M$^{III}$]$\text{C}_2\text{O}_4$]$\times$- paramagnetic anions can be identified in the title family, namely, with monoclinic, orthorhombic and triclinic symmetry. Metallic and superconducting crystals dominate among the salts of the monoclinic series with a $\beta'$ packing type of the conducting BEDT-TTF layers (M$^{III}$ is Fe, Cr; A' is H$_3$O\textsuperscript{+} or NH$_4$\textsuperscript{+}; G–different solvents), the superconducting transition temperature ($T_C$) being dependent on G molecule size.\textsuperscript{5,6,12,17} In addition, $\beta'$-salts containing mixtures of the guest solvents benzonitrile and pyridine in different mole fractions are known: $\beta'$(BEDT-TTF)$_2$H$_2$[Fe(C$\text{C}_2$O$_4$)$_3$]·(PhCN)$_x$(C$_6$H$_5$N)$_{1-x}$.\textsuperscript{16} It was found that the $T_C$ of these crystals depends on a proportion of two solvents in the anion layer and it decreases with an increasing degree of substitution of benzonitrile molecules for pyridine ones.

The orthorhombic series involves three semiconductors (M$^{III}$ is Fe$^{III}$, A' is K$^+$ or NH$_4$\textsuperscript{+}; M$^{III}$ is Cr$^{III}$, A' is H$_3$O\textsuperscript{+} or G = PhCN) with ‘pseudo-$\alpha'$-packing of the differently charged donor layers: (BEDT-TTF)$_2$+ dimers are surrounded by neutral (BEDT-TTF)$^+$ monomers.\textsuperscript{1,4}

The triclinic series (M$^{III}$ is Fe$^{III}$, A' is NH$_4$\textsuperscript{+}) involves three compounds with asymmetric, including chiral, guest molecules.\textsuperscript{1,14} As a result of a non-equivalence arrangement of solvent molecules with respect to neighbouring donor layers, $\alpha$ and $\beta'$ conducting layers alternate in these crystals. A metal–semiconductor transition at ~150 K is observed in the crystals comprising PhCOH(H)CH$_3$, while the crystals with PhCOCH$_3$ are semiconductors.

A comparative analysis of this family of crystals shows that guest solvent molecules do not only have a template function. The solvent nature noticeably affects the structure and (super)conducting properties of the (BEDT-TTF)$_4$H$_2$[Fe(C$\text{C}_2$O$_4$)$_3$]·G crystals. The goal of the present work was to further investigate
these effects by introducing different guest molecules into the hexagonal anion network.

It is known that the formation of different phases in the (BEDT-TTF)$_2$[M$^{III}$(C$_2$O$_4$)$_3$]$\cdot$G family depends on components of electrochemical synthesis, “dry” solvents provide the growth of crystals of orthorhombic phases and to prepare crystals of monoclinic and triclinic phases one should add a small amount of water.\textsuperscript{1,3,4} We found that crystals of monoclinic (superconducting and metallic) phases can be prepared using a mixture of 96% ethanol, 1,2,4-trichlorobenzene (1,2,4-TCB) (or 1,3-dibromobenzene-1,3-DBB) and different solvents (benzonitrile, BN, fluorobenzene, FB, chlorobenzene, CB, 1,2-dichlorobenzene, 1,2-DCB, bromobenzene, BB or nitrobenzene, NB) as the electrocrystallization medium.

Using this approach, a number of known and new BEDT-TTF salts with the tris(oxalato)ferrate anion have been synthesized. Among the new compounds there are salts of the known monoclinic and orthorhombic series, with two solvent molecules mixed in the anion layer, as well as a novel bi-layered triclinic phase of the family incorporating 1,2-dibromobenzene (1,2-DBB) and monoclinic crystals, \(\alpha\)-(BEDT-TTF)$_2$[Fe(C$_2$O$_4$)$_3$]$\cdot$X, of another stoichiometry. Single-crystal X-ray structural study of the crystals was performed. The relationships between the crystal structures and their conducting properties were analyzed.

**Experimental**

**Synthesis**

BEDT-TTF, (NH$_4$)$_3$[Fe(C$_2$O$_4$)$_3$]$\cdot$3H$_2$O, BN, NB, BB, CB, FB, 1,2-DCB, 1,2-DBB, 1,3-DBB and 1,2,4-TCB were used as received (Aldrich). 18-crown-6 (Aldrich) was purified by recrystallization from acetonitrile and dried under vacuum at 30 °C over P$_2$O$_5$.

Electrocrystallization of the charge transfer salts was performed in conventional two-compartment H-shaped cells with Pt wire electrodes at a constant current of 0.5–0.75 μA and at a fixed temperature (25 °C). Saturated solutions of BEDT-TTF and the electrolyte (NH$_4$)$_3$[Fe(C$_2$O$_4$)$_3$]$\cdot$3H$_2$O were used to keep constant concentrations of the reagents. Electrooxidation of BEDT-TTF was carried out using mixtures of different solvents. The reagents were dissolved in one compartment of the cell and then the obtained solution was assigned between the two compartments.

The obtained salts (I–XII) and compositions of corresponding mixtures of solvents are listed in Table 1. Below we cite the description of the synthesis of $\beta$'-(BEDT-TTF)$_2$H$_2$O[Fe(C$_2$O$_4$)$_3$]$\cdot$(BN0.35CB0.65)$_2$X (X) as an example for obtaining monoclinic crystals (a), as well as syntheses of $\alpha$-'pseudo-$\kappa$'-(BEDT-TTF)$_2$H$_2$O[Fe(C$_2$O$_4$)$_3$]$\cdot$(1,2-DBB) (XII) (b) and $\alpha$- (BEDT-TTF)$_2$[Fe(C$_2$O$_4$)$_3$]$\cdot$X (XIII) (c).

(a) 15 mg of BEDT-TTF, 150 mg of mixture of (NH$_4$)$_3$[Fe(C$_2$O$_4$)$_3$]$\cdot$3H$_2$O and 450 mg of 18-crown-6 dissolved in a mixture of solvents (20 mL of 1,2,4-TCB, 5 mL of BN, 5 mL of CB and 3 mL EtOH) were put in the cathodic compartment of the electrochemical cell pre-blown by argon for 10 min. The reaction mixture was stirred for 4 h upon heating in argon atmosphere. Then the solution was distributed between the compartments of the cell, the electrodes were put in each compartment and the cell was placed in a thermostat. Single crystals were obtained as thick plates after 2 weeks at a constant current of 0.5 μA.

(b) 10 mg of BEDT-TTF, 200 mg of (NH$_4$)$_3$[Fe(C$_2$O$_4$)$_3$]$\cdot$3H$_2$O and 300 mg of 18-crown-6 in a mixture of solvents (15 mL of 1,2-DBB and 2 mL of EtOH), $I = 0.75$ μA.

(c) 15 mg of BEDT-TTF, 200 mg of (NH$_4$)$_3$[Fe(C$_2$O$_4$)$_3$]$\cdot$3H$_2$O, and 300 mg of 18-crown-6 in a mixture of solvents (15 mL of 1,2,4-TCB and 5 mL of EtOH), $I = 0.75$ μA.

**2.2. X-Ray diffraction**

An X-ray structural study was performed on single crystals of I–IV and VII–XIII at room temperature using an Oxford Diffraction Gemini-R diffractometer equipped with a Ruby CCD detector and two (Cu and Mo) X-ray tubes. The unit cell parameters were measured with Cu-Kα radiation ($\lambda$(Cu-Kα) = 1.54178 Å) by short data collections at an enlarged crystal-to-detector distance (80 mm). Complete experimental data collections were performed on some of the crystals using Mo-Kα radiation ($\lambda$(Mo-Kα) = 0.71073 Å, graphite monochromator, omega-scans). Data reduction with empirical absorption correction of the experimental intensities (Scale3AbsPack program) was made with the CrysalisPro software.\textsuperscript{18}

The structures were solved by a direct method followed by Fourier syntheses and refined by a full-matrix least-squares method using the SHELX-97 programs\textsuperscript{19} in an anisotropic approximation for all non-hydrogen atoms except for components of disordered solvent molecules (Cl and Br atoms of CB and BB solvents were made anisotropic in the structures III and XI only). H-atoms in BEDT-TTF and solvent molecules were placed in idealized positions and refined using a riding model, $U_{	ext{iso}}$(H) were fixed at 1.2$U_{	ext{eq}}$(C). In the H$_2$O$^+$ cations, which are located inside the anion layer and disordered in the monoclinic and orthorhombic phases between two equi-probable positions near the twofold $\gamma$ axis, O–H bonds were restrained to be of the same length by SADI or DFIX instructions, $U_{	ext{iso}}$(H) were specified as 1.5$U_{	ext{eq}}$(O). The positions of the mixed solvent molecules were separated: the BN molecule lay exactly on a twofold axis, while the second solvent molecule occupied two equi-probable positions near this axis. Isotropic thermal parameters $U_{	ext{iso}}$ for all non-hydrogen atoms in both solvents had one common value which was refined together with occupation factors of one and another solvent molecules as linked variables $x$ and $(1-x)$. The resulting solvent compositions are listed in Table 1.

Table 2 shows details of experimental data collections and structure refinements for crystals I–IV, VII, VIII, IX–XI. The X-ray data for crystals VIII and VIIIa containing a (BN)$_{0.8}$(NB)$_{0.2}$ mixture show lower quality. Thus, the refinement data are not included in Table 2. The complete structural data for the novel $\alpha$- ‘pseudo-$\kappa$'- (BEDT-TTF)$_2$H$_2$O[Fe(C$_2$O$_4$)$_3$]$\cdot$(1,2-DBB) phase (triclinic, $a = 10.333(1)$, $b = 19.817(2)$, $c = 36.876(3)$ A, $\alpha = 86.938(7)$, $\beta = 89.387(7)$, $\gamma = 89.720(7)$, $V = 7540(1)$ A$^3$, $P1$, $Z = 4$) will be published elsewhere. The $\alpha$- (BEDT-TTF)$_2$[Fe(C$_2$O$_4$)$_3$]$\cdot$X (XIII) crystals (monoclinic, $a = 11.132(1)$, $b = 12.573(2)$, $c = 37.729(4)$ A, $\alpha = 96.34(1)$, $\beta = 65.073(1)$, $\gamma = 89.260(1)$, $V = 5248.3(9)$ A$^3$, $P2_1$, $Z = 2$) are unstable and the structure of their anion layer cannot be defined reliably.
Table 1  List of the (BEDT-TTF) \textsubscript{4}H\textsubscript{3}O[Fe\textsuperscript{III}(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}]\textsuperscript{-}\textsuperscript{G} radical cation salts obtained and their conducting properties

<table>
<thead>
<tr>
<th>Salt</th>
<th>G, mole fractions\textsuperscript{a}</th>
<th>S, volume ratio\textsuperscript{b}</th>
<th>Symmetry</th>
<th>BEDT-TTF packing</th>
<th>Conducting properties\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>BN</td>
<td>1.3-DBB/BN = 2.5 : 1</td>
<td>C2/c</td>
<td>β\textsuperscript{''}</td>
<td>T\textsubscript{c} = 6.5 K</td>
</tr>
<tr>
<td>II</td>
<td>BN</td>
<td>TCB/BN = 5 : 1</td>
<td>C2/c</td>
<td>β\textsuperscript{''}</td>
<td>T\textsubscript{c} = 7.4 K</td>
</tr>
<tr>
<td>III</td>
<td>CB</td>
<td>TCB/CB = 4 : 1</td>
<td>C2/c</td>
<td>β\textsuperscript{''}</td>
<td>M &gt; 4.2 K</td>
</tr>
<tr>
<td>IV</td>
<td>FB</td>
<td>TCB/FB = 2 : 1</td>
<td>C2/c</td>
<td>β\textsuperscript{''}</td>
<td>M &gt; 1.5 K</td>
</tr>
<tr>
<td>V</td>
<td>BB</td>
<td>TCB/BB = 1 : 1</td>
<td>C2/c</td>
<td>β\textsuperscript{''}</td>
<td>M\textsuperscript{d} &gt; 4.2 K</td>
</tr>
<tr>
<td>VI</td>
<td>1,2-DCB</td>
<td>TCB/DCB = 1 : 3</td>
<td>C2/c</td>
<td>β\textsuperscript{''}</td>
<td>M &gt; 1.5 K</td>
</tr>
<tr>
<td>VII</td>
<td>(BN)\textsubscript{0.03}(DCB)\textsubscript{0.14}</td>
<td>TCB/BN/DCB = 4 : 1 : 1</td>
<td>C2/c</td>
<td>β\textsuperscript{''}</td>
<td>T\textsubscript{c} = 7.2 K</td>
</tr>
<tr>
<td>VIIa</td>
<td>(BN)\textsubscript{0.03}(DCB)\textsubscript{0.12}</td>
<td>TCB/BN/DCB = 4 : 1 : 1</td>
<td>Phon</td>
<td>'pseudo-κ'</td>
<td>Sm</td>
</tr>
<tr>
<td>VIII</td>
<td>(BN)\textsubscript{0.5}(NB)\textsubscript{0.5}</td>
<td>TCB/BN/NB = 2 : 1 : 1</td>
<td>C2/c</td>
<td>β\textsuperscript{''}</td>
<td>T\textsubscript{c} = 6.6 K</td>
</tr>
<tr>
<td>VIIIa</td>
<td>(BN)\textsubscript{0.5}(NB)\textsubscript{0.5}</td>
<td>TCB/BN/NB = 2 : 1 : 1</td>
<td>Phon</td>
<td>'pseudo-κ'</td>
<td>Sm</td>
</tr>
<tr>
<td>IX</td>
<td>(BN)\textsubscript{0.60}(FB)\textsubscript{0.5}</td>
<td>TCB/BN/FB = 2 : 1 : 1</td>
<td>C2/c</td>
<td>β\textsuperscript{''}</td>
<td>T\textsubscript{c} = 6.0 K</td>
</tr>
<tr>
<td>X</td>
<td>(BN)\textsubscript{0.65}(CB)\textsubscript{0.35}</td>
<td>TCB/BN/CB = 4 : 1 : 1</td>
<td>C2/c</td>
<td>β\textsuperscript{''}</td>
<td>T\textsubscript{c} = 6.9 K</td>
</tr>
<tr>
<td>XI</td>
<td>(BN)\textsubscript{0.83}(BB)\textsubscript{0.83}</td>
<td>TCB/BN/BB = 1 : 2 : 1</td>
<td>C2/c</td>
<td>β\textsuperscript{''}</td>
<td>T\textsubscript{c} = 4.2 K</td>
</tr>
<tr>
<td>XII</td>
<td>1,2-DBB</td>
<td>1,2-DBB</td>
<td>P1</td>
<td>α-'pseudo-κ'</td>
<td>M &gt; 1.5 K</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Composition and mole fractions of the guest solvents (G) obtained from X-ray structure refinement data.
\textsuperscript{b} Volume ratios of solvents (S) in the electrochemical syntheses. In each case EtOH was also added (10–15 v %).
\textsuperscript{c} T\textsubscript{c} = temperature for an onset of superconducting transition; M = metal (for details see text, part 3.3). Sm = semiconductor.
\textsuperscript{d} A superconducting transition in β\textsuperscript{''}-(BEDT-TTF)\textsubscript{4}H\textsubscript{3}O[Fe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}]\textsuperscript{-}BB crystals was observed below 4.0 K in ref. 11.

### 2.3. Conductivity measurements

The temperature dependencies of the electrical resistance of the single crystals were measured under constant current by a standard four-probe technique. Measurements were performed along the c*-axis running perpendicular to the conducting layers. A crystal was glued with conducting graphite paste to four platinum wires, 15 μm in diameter, fastened on the measuring module. The temperature change rate was about 1 K min\textsuperscript{-1}.

In test experiments, the dynamic susceptibility of the β\textsuperscript{''}-(BEDT-TTF)\textsubscript{4}H\textsubscript{3}O[Fe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}]\textsuperscript{-}BB crystal was glued with conducting graphite paste to four platinum wires, 15 μm in diameter, fastened on the measuring module. The temperature change rate was about 1 K min\textsuperscript{-1}.

### 3. Results and discussion

#### 3.1 Synthesis

The electrochemical syntheses in the system of BEDT-TTF with the metal oxalate anion [Fe\textsuperscript{III}(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}]\textsuperscript{-} were performed using a modified procedure. A commonly adopted way for obtaining the title compounds provides for electrocrystallization in an organic solvent G, sometimes with the addition of a few drops of water. The modified procedure for the synthesis differs from the usual one in that a water–ethanol azeotropic mixture (96% water). The modified procedure for the synthesis differs from the usual one in that a water–ethanol azeotropic mixture (96% water). The modified procedure for the synthesis differs from the usual one in that a water–ethanol azeotropic mixture (96% water). The modified procedure for the synthesis differs from the usual one in that a water–ethanol azeotropic mixture (96% water).

The solubility of the electrolyte, i.e. to increase its concentration in the reaction medium, is not a necessary condition for the formation of the monoclinic phases. Therefore, the main role of water in the syntheses of the monoclinic crystals is probably to enhance the solubility of the electrolyte, i.e. to increase its concentration in the reaction medium. The electrolyte (NH\textsubscript{4})\textsubscript{3}Fe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}:3H\textsubscript{2}O dissolves well in DMF and the reaction proceeds in the absence of water. For the electrochemical syntheses of the monoclinic crystals in such solvents as FB, CB and others in which the electrolyte is weakly soluble, the water additives are necessary. However, there are certain difficulties in mixing water with organic solvents. The mixtures obtained are unstable and segregate with time into organic and water layers. As a result, a major portion of the (NH\textsubscript{4})\textsubscript{3}Fe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}:3H\textsubscript{2}O electrolyte passes from the organic layer to the water one and the formation of the orthorhombic phases becomes favourable in the organic medium. Electrocrystallization does not occur in solvents which weakly dissolve the electrolyte and do not mix with water (1,2-DCB, 1,2-DBB, etc.). In such cases the concentration of the electrolyte in the solution can be increased by adding 96% EtOH. Previously we have used ethanol to synthesize the β\textsuperscript{''}-phase with 1,2-DCB.

In the present work, EtOH has been used successfully in combination with different organic solvents (G) to prepare the crystals I–XII of the family (see the footnotes to Table 1). For comparison, the electrocrystallization in a CB and H\textsubscript{2}O mixture proceeded for two months at a very low current because of the low concentration of the electrolyte and yielded small irregular-shaped crystals unsuitable for physical measurements. The use of CB and EtOH essentially increased the concentration of the electrolyte and large isometric single crystals were obtained within 10–12 days. The use of a 1,2-DBB and EtOH mixture provided the preparation of crystals of the novel triclinic phase (XII). When using 1,2-4-TCB, in which the electrolyte is almost insoluble, the amount of ethanol in the mixture was increased up to 25 v %. These conditions lead to the formation of the

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Table 2. Crystal structure data of the I–IV, VIIa, VIII, and IX–XII salts in the (BEDT-TTF) 3Fe(C 2 O 4 ) 3 − ]X crystal family. Complete X-ray diffraction experiments have been done at room temperature using Mo-Kα radiation (λ = 0.71073 Å), unit cell parameters were refined with Cu-Kα (λ = 1.54178 Å).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Formula</th>
<th>Space group</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>β/°</th>
<th>V/Å³</th>
<th>Z</th>
<th>ρ/ρ m</th>
<th>ρ m/ρ 0</th>
<th>R 1</th>
<th>wR 2</th>
<th>Goodeiness-fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (BN)</td>
<td>C 37.86H 39.86Cl 0.28</td>
<td>Monoclinic</td>
<td>10.2650(6)</td>
<td>10.2615(5)</td>
<td>35.216(2)</td>
<td>92.726(5)</td>
<td>7275.8(7)</td>
<td>1</td>
<td>0.8490</td>
<td>0.0411</td>
<td>0.0431</td>
<td>0.0390</td>
<td>0.2968</td>
</tr>
<tr>
<td>II (BB)</td>
<td>C 37.88H 39.88Cl 0.24</td>
<td>Monoclinic</td>
<td>10.2854(4)</td>
<td>10.3011(5)</td>
<td>35.367(2)</td>
<td>93.089(3)</td>
<td>7269.1(6)</td>
<td>1</td>
<td>0.8490</td>
<td>0.0378</td>
<td>0.0378</td>
<td>0.0412</td>
<td>0.3148</td>
</tr>
<tr>
<td>III (CB)</td>
<td>C 37.35H 40Cl 0.65</td>
<td>Monoclinic</td>
<td>10.2877(7)</td>
<td>10.3011(5)</td>
<td>36.096(3)</td>
<td>92.567(5)</td>
<td>7264.9(7)</td>
<td>1</td>
<td>0.8490</td>
<td>0.0461</td>
<td>0.0461</td>
<td>0.0521</td>
<td>0.3148</td>
</tr>
<tr>
<td>IV (FB)</td>
<td>C 37.17H 40Br 0.83</td>
<td>Monoclinic</td>
<td>10.4247(7)</td>
<td>10.3011(5)</td>
<td>35.255(2)</td>
<td>92.496(5)</td>
<td>7271(1)</td>
<td>1</td>
<td>0.8490</td>
<td>0.0471</td>
<td>0.0471</td>
<td>0.0521</td>
<td>0.4591</td>
</tr>
</tbody>
</table>

Effect of 1,2,4-TCB and 1,3-DBB. It should be noted that the addition of ethanol to the reaction mixture does not always provide the formation of high quality monoclinic single crystals of the family. In particular, in the BN and EtOH mixture the monoclinic crystals appear as thin plates of low quality. It was found that adding 1,2,4-TCB or 1,3-DBB into the mixture of EtOH and solvent G (BN, NB, FB, CB, BB, DCM) results in the formation of quite good bulk crystals of the β-phase (Table 1). 1,2,4-TCB and 1,3-DBB are not involved in the composition of the crystals formed. Nevertheless, they play an important role in the electrochemical synthesis since reproducibility and selectivity of the syntheses and crystal quality noticeably increase.

It should be mentioned that when synthesizing one of monoclinic salts of the family, β-(BEDT-TTF) 3H 2 O[Cr(C 2 O 4 ) 3 ]− DCM, the authors followed a similar method and used a mixture of dichloromethane (DCM) with acetonitrile (AN) and 2-chloropyridine. They noticed that though the latter component was not involved in the composition of the crystals, its presence was necessary since it allowed the preparation of a few very thin single crystals. When an identical mixture, but without the 2-chloropyridine, was used in the same conditions no crystals were formed. Other inspiring results have been obtained recently by adding a chiral R-carvone solvent during the usual electrocrystallization of BEDT-TTF with the tris(oxalato)chromate(III) anion in a nitromethane (NM) or DCM/AN mixture. Though the resulting salts (BEDT-TTF) 3Na[Cr(C 2 O 4 ) 3 ]− G (G = NM or DCM) differ by stoichiometry from the title family, they deserve a mention as the first chiral salts, comprising predominantly one enantiomer of [Cr(C 2 O 4 ) 3 ] 3− , crystallized from a solution of a racemic anion in the chiral solvent.

Using the modified procedure of electrochemical synthesis, we considerably extended the number of family members and obtained a series of crystals suitable for X-ray and physical measurements (Table 1).

The ability of different solvents to occupy the hexagonal cavity. New monoclinic charge-transfer salts containing the molecules of two guest solvents in the anion layer, (G1) (G2) − , where G1 = BN, G2 = FB, CB, BB, NB, 1,2-DCB (VII–XI, Table 1), were synthesized. It was found that the degree of substitution of the BN molecules in the structure is mainly defined by the nature of G2. These experiments allowed us to compare the ability of different solvents to occupy the hexagonal cavity. It is seen from the data presented in Table 1 that FB, CB and BB enter into the structure more easily than the BN molecules. If the solvent mixture contains equal volumes of BN and CB (or BN and FB), this approximately corresponds to their equal molar ratio, then the resulting crystals X and IX contain 35% and 40% of BN, respectively. The BB molecules enter in the anion layer more easily than the CB ones, even at a twofold excess of BN relative to BB (XI) the crystals only contain 17% of BN. NB and 1,2-DCB are less involved in the structure than BN. At an equal ratio of BN : 1,2-DCB or BN : NB in the mixtures, only 20% of NB (VIII) and 14% of 1,2-DCB (VII) are found in the structures.
Thus, the ability to occupy the hexagonal cavity grows in the order: 1,2-DCB, NB, BN, FB, CB, BB. The efforts to obtain crystals in which a part of the BN molecules is substituted by G2 = 1,3-DBB failed. The resulting crystals contain BN only (I, Table 1).

3.2. Structure

A detailed X-ray diffraction study of the single crystals and a comparative analysis of the new structural data led to several important conclusions.

Role of 1,2,4-TCB and 1,3-DBB solvents from the structural point of view. It was found that the large solvent molecules 1,2,4-TCB and 1,3-DBB, used in all of the reactions I–XI, are not involved in the composition of the crystals. An obvious reason for this is that these solvent molecules are too large to fit in the hexagonal cavity of the anionic layer in the monoclinic crystals of the (BEDT-TTF)$_4$A$^+$(C$_2$O$_4$)$_3$$^-$G family. The molecular volumes of TCB and DBB were estimated from the CCDC structural data for pure solvents$^{22,23}$ using the formula $V_{\text{unit cell}}/Z$. It should be noted that only the structures of 1,3,5-TCB and 1,4-DBB modifications were found in the database. However, it is clear that the difference in halogen atom positions does not noticeably affect the volume of the molecules, taking into account their close packing in the structure. The calculated volumes of DBB and TCB are ~170 and 180 Å$^3$, respectively, which is higher than the volume of 1,2-DCB (160 Å$^3$) which is today the largest guest molecule in the anion layer of the monoclinic phases.

Thus, both DBB and TCB molecules are too large to be included into the 2D anion layer without a destructive effect on the hexagonal anion network and/or the BEDT-TTF environment. These effects are well pronounced in the reactions for XII and XIII, where only the large 1,2-DBB and 1,2,4-TCB solvents with EtOH were used, which leads to the formation of other phases. When mixtures of 1,2,4-TCB (or 1,3-DBB) with solvents with smaller molecules were used, only the latter were found in the composition of the anion layer (I–XI, Table 1).

Note that most of prepared crystals show an unusual morphology (Fig. 1). They have a shape of thick plates or parallelepipeds, the largest face of the plate being perpendicular to the conducting layers (usually in BEDT-TTF salts conducting layers are parallel to the plate).

Due to the good quality single crystals obtained by the modified procedure of synthesis, some new structural features of the monoclinic compounds of the title family have been identified.

H$_3$O$^+$ and solvent disordering in the monoclinic $\beta'$-(BEDT-TTF)$_4$H$_3$O[Fe(C$_2$O$_4$)$_3$]-G crystals. Fig. 2 shows the general view of the structure of the monoclinic crystals. In all of the crystals investigated hydroxonium ions were successfully localized. Moreover, it was found that they are disordered in two equiprobable positions relative to a twofold axis (Fig. 3a). As a result, each hydrogen atom of the hydroxonium ion is shifted away from the position equidistant from the two outer oxygen

![Fig. 1](image1.png)  
(a)  
(b)  
(c)  

Fig. 1 Photo images of the crystals II (G = BN) and IX (G = (BN)$_{0.40}$(FB)$_{0.60}$), taken during the X-ray experiment, which indicate unusual crystal morphology with $b^*$ normal to the plate plane, (a) reciprocal axes orientation and face indices for II, (b) growth stripes on (010) crystal face of II, (c) orientation and faces for the crystal IX.

![Fig. 2](image2.png)  

Fig. 2 $\beta'$-(BEDT-TTF)$_4$H$_3$O[Fe(C$_2$O$_4$)$_3$]-G (X) structure projected along $a$. 

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hydrogen bonds. Each contacting with opposite surfaces of the anion layer by O–H contacting.

The geometry of hydrogen bonds formed between H$_3$O$^+$ and anion surrounding in the structure is characteristic of the H$_3$O$^+$ ion has trigonal pyramid geometry with the oxygen atom at its vertex. For one of the two orientations of H$_3$O$^+$, all O$_{H3O}$–H···O$_{an}$ contacts are directed towards the oxygen atoms lying on one side of the anion layer and for the other orientation, all of the contacts are directed towards the oxygen atoms on the opposite side (Fig. 3b).

Disorder of the solvent molecules was also found in all monoclinic salts and characterized. Though twofold axial symmetry is an intrinsic property of all of the guest solvent molecules (G) listed in Table 1, in the anion layer they occupy two equi-probable sites near a twofold crystal axis, each one being connected by hydrogen contacts with the oxalate environment (Fig. 3a). In the crystals with a single guest molecule (I–VI), disorder of different degrees is observed for all of the solvents including BN (Fig. 4a). For the monoclinic crystals with mixed solvents (VII–XI), the BN molecule was refined as fully ordered and for other molecules (G2) disordering relative to the twofold axis was observed as in the phases comprising one solvent. As a result, three different positions of the G molecules were located in each cavity (see Fig. 4b and c).

The room-temperature disorder in both of the terminal ethylene groups of one of the two independent BEDT-TTF molecules is characteristic of the β$^*$-salts of the family and is observed in all of the monoclinic crystals listed in Table 1. The degree of disorder is nearly the same in all of the superconducting crystals and a ratio of the two orientations in each disordered layer is nearly the same in all of the superconducting crystals and a ratio of the two orientations in each disordered layer is nearly the same in all of the superconducting crystals and a ratio of the two orientations in each disordered layer is nearly the same in all of the superconducting crystals and a ratio of the two orientations in each disordered layer is nearly the same in all of the superconducting crystals and a ratio of the two orientations in each disordered layer is nearly the same in all of the superconducting crystals and a ratio of the two orientations in each disordered layer is nearly the same in all of the superconducting crystals and a ratio of the two orientations in each disordered layer

New and novel (BEDT-TTF)$_2$H$_2$O[Fe(C$_2$O$_4$)$_3$]–G phases. Both the known salts of monoclinic symmetry with BN, CB, BB, FB and DCC and DCB (crystals I–VI) and new crystals of monoclinic and orthorhombic series with mixed solvents (VII–XI) were synthesized. Moreover, novel phases (XII, XIII) were obtained. The real ratios of the solvents in crystals VII–XI (see column 2 in Table 1) were found and refined from single-crystal X-ray structural data.

The concurrent growth of crystals with two polymorphic modifications (monoclinic superconducting and orthorhombic semiconducting) was found in two reactions with mixed solvents (VII and VII, VIII and VIII, Table 1). A similar phenomenon of concomitant polymorphism with the formation of β$^*$ and ‘pseudo-κ’ phases was previously observed in reactions with BN and H$_2$O.

The formation of novel phases was revealed when only the large solvents 1,2-DBB or 1,2,4-TCB with EtOH were used in the syntheses (XII and XIII in Table 1). The projection of structure XII is shown in Fig. 5. Remarkably, 1,2-DBB is involved in the structure. The new salt, κ-‘pseudo-κ’-(BEDT-TTF)$_2$H$_2$O[Fe(C$_2$O$_4$)$_3$]–(1,2-DBB), which has triclinic $P1$ symmetry is a novel phase in the title family. It was found that 1,2-DBB, which is more compact than 1,3-DBB due to a closer arrangement of Br atoms, is still able to enter into the hexagonal cavity. However, although the resulting anion layer keeps a honeycomb-like structure, it no longer fits into the β$^*$-layer of the BEDT-TTF. The latter has to adjust the donor arrangement in accordance with the modified anion network. Two packing motifs, κ and ‘pseudo-κ’, appeared to be convenient in translation parameters.

<table>
<thead>
<tr>
<th>H-bond</th>
<th>D–H/Å</th>
<th>H···A/Å</th>
<th>D···A/Å</th>
<th>D–H···A/˚</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(51)–H(51a)–O(4)$^*$</td>
<td>1.17(3)</td>
<td>1.71(3)</td>
<td>2.874(4)</td>
<td>173(5)</td>
</tr>
<tr>
<td>O(51)–H(51b)–O(6)$^*$</td>
<td>1.17(4)</td>
<td>1.70(4)</td>
<td>2.82(5)</td>
<td>158(5)</td>
</tr>
<tr>
<td>O(51)–H(51c)–O(5)$^*$</td>
<td>1.17(3)</td>
<td>1.67(4)</td>
<td>2.82(6)</td>
<td>169(4)</td>
</tr>
</tbody>
</table>

| Symmetry operations: (i) 0.5–x, y–0.5, 1.5–z; (ii) 1–x, y, 1.5–z; (iii) –x, y, 1.5–z. |
structure projected along $a$.

It is the first time that a radical cation salt with alternating conducting layers of $\alpha$ and ‘pseudo-\(\kappa\)' type of molecular packing has been prepared. This is the second phase in the title family, which is infrequently observed in organic conductors. A series of bilayered triclinic salts, $\alpha$-‘\(\kappa\)'-(BEDT-TTF)$_4$H$_3$O[Fe(C$_2$O$_4$)$_3$]-G, comprising asymmetric guest solvent molecules in the anion layer was described earlier.\(^{13,14}\) In the new $\alpha$-‘\(\kappa\)' phase XII, as in $\alpha$-\(\beta\')-\(\kappa\)' crystals, each large solvent molecule is located asymmetrically with respect to two neighbouring BEDT-TTF layers. Both Br atoms in the dibromo-benzene molecule (shown by black circles in Fig. 5) are directed toward the $\alpha$-layer.

As a result, the two BEDT-TTF layers are non-equivalent in their structure, charge state and conductivity. In the ‘pseudo-\(\kappa\)’ layer of the mixed $\alpha$-‘pseudo-\(\kappa\)' phase, the same charge separation as in the structure of pure ‘pseudo-\(\kappa\)’ orthorhombic salts of the family is found. (BEDT-TTF)$_2$H$_3$O[Fe(C$_2$O$_4$)$_3$]-FB crystals. A metallic behaviour of this salt is observed down to 100–150 K, followed by slow resistance growth down to 1.5 K without a superconducting transition. A similar R(T) dependence with a very broad transition to activated conductivity is observed for $\beta\)'-(BEDT-TTF)$_4$H$_3$O[Fe(C$_2$O$_4$)$_3$]-FB crystals. A metallic behaviour of this salt is observed down to 100–150 K, followed by slow resistance growth down to 1.5 K without a superconducting transition. A similar R(T) dependence with a very broad transition to activated conductivity is observed for $\beta\)'-(BEDT-TTF)$_4$H$_3$O[Fe(C$_2$O$_4$)$_3$]-FB crystals.

Fig. 6 The temperature dependencies of normalized interlayer resistance for the $\beta\)'-(BEDT-TTF)$_4$H$_3$O[Fe(C$_2$O$_4$)$_3$]-G crystals, measured down to 4.2 K. G = BB (V), DCB (VI), (BN)$_{0.34}$DCB$_{0.14}$ (VII), (BN)$_{0.3}$NB$_{0.2}$ (VIII), (BN)$_{0.4}$FB$_{0.6}$ (IX), (BN)$_{0.35}$CB$_{0.65}$ (X), (BN)$_{0.17}$BB$_{0.83}$ (XI). The insert shows the superconducting transition for the $\beta\)'-(BEDT-TTF)$_4$H$_3$O[Fe(C$_2$O$_4$)$_3$]-BN crystals (XI), registered by measurement of ac susceptibility.

Fig. 5 $\alpha$-‘\(\kappa\)'-(BEDT-TTF)$_4$H$_3$O[Fe(C$_2$O$_4$)$_3$]-1,2-DBB (XII) structure projected along $a$. 

3.3 Conducting properties

Table 1, Fig. 6 and Fig. 7 show the conducting properties of the crystals (I–XII). Among them there are superconductors, metals and semiconductors.

The conducting properties of the $\beta\)'$-phases comprising only one solvent in the structure (I–VI) are similar to those described earlier.\(^{1-12}\) However, no superconducting transition, as declared in ref. 25, was found by us in the $\beta\)'$-(BEDT-TTF)$_4$H$_3$O[Fe(C$_2$O$_4$)$_3$]-FB crystals. A metallic behaviour of this salt is observed down to 100–150 K, followed by slow resistance growth down to 1.5 K without a superconducting transition. A similar R(T) dependence with a very broad transition to activated conductivity is observed for $\beta\)'-(BEDT-TTF)$_4$H$_3$O[Fe(C$_2$O$_4$)$_3$]-FB crystals.

The structure of the anion layer in these crystals is strongly different from that of the described family. Instead of hexagonal anion networks, isolated tri(oxyalate)ferrate anions appear, surrounded by hydrogen-bonded chains of water molecules. In spite of different cell parameters and symmetry, the arrangement of the anions is similar in all three $\alpha$-phases.

Most probably, small ethanol or water molecules are involved as a solvent. The conducting layer of the crystals has an $\alpha$-type of BEDT-TTF arrangement. The structure of the anion layer cannot be determined reliably because of crystal instability. Most probably, small ethanol or water molecules are involved into the anion layer and can easily escape from the crystal, which destroys the structure. The new phase cannot be attributed to the (BEDT-TTF)$_4$H$_3$O[Fe$^{III}$(C$_2$O$_4$)$_3$]-G family because of another crystal stoichiometry, the BEDT-TTF to anion ratio in XIII is $6 : 1$. It should be noted that two phases with the $\alpha$-type of conducting layers have already been found among the salts with metal oxalate anions, both having $6 : 1$ stoichiometry. They have a common formula (BEDT-TTF)$_4$H$_3$O[Fe(C$_2$O$_4$)$_3$]$n$(H$_2$O)$_m$, and contain a great amount of water (for the two phases, $n = 15$ and 16).\(^{24}\) The structure of the anion layer in these crystals is strongly different from that of the described family. Instead of hexagonal anion networks, isolated tri(oxyalate)ferrate anions appear, surrounded by hydrogen-bonded chains of water molecules. In spite of different cell parameters and symmetry, the arrangement of the anions is similar in all three $\alpha$-phases.
reveal Shubnikov-de Haas quantum oscillations.\(^8,^{26,27}\) This shows that insulating and metallic states coexist in these salts. An intrinsic tendency to disorder in the anion layers and/or in the ethylene groups of the BEDT-TTF molecules, as well as some charge ordering, is responsible for the electronic inhomogeneity in the \(\beta'\)-salts.\(^{15,27}\) A charge disproportionate state in \(\beta''\)-BEDT-TTF\(_4\)H\(_2\)O[Fe(C\(_2\)O\(_4\))\(_3\)]-PhNO\(_2\) was found by means of Raman spectroscopy at a temperature just above the insulator-superconductor transition.\(^{29}\)

The relationship between the dielectric instabilities in these salts and the appearance of superconductivity was discussed earlier.\(^{15,27}\) It was pointed out that the mechanism of superconductivity in the \(\beta''\)-salts can be a charge-fluctuation-mediated one proposed by Merino and McKenzie.\(^30\) Some our results also testify to the fact that the coexistence of metallic and insulating states is an important prerequisite for superconductivity in the \(\beta''\)-(BEDT-TTF)\(_4\)H\(_2\)O[Me(C\(_2\)O\(_4\))\(_3\)]-G crystals. For instance, a sample of the \(\beta''\)-salt with \(M = Fe\) and \(G = DMF\) showing resistivity below 50 \(K\) exhibits a superconducting transition near 2 \(K\), whereas the samples with \(M = Cr\) and \(G = DMF\) showing metallic behaviour in the whole temperature range \((R_{1,2}/R_{RT} \sim 10^{-2})\) do not transform into a superconducting state.\(^7\) Another example is the \(\beta''\)-salt with 1,2-DCB as the guest solvent and \(M = Fe\), which shows robust metallic behaviour without a superconducting transition down to 1.5 \(K\) (Fig. 6).\(^{12}\) The temperature dependencies of the resistivity of the crystals with mixed solvents \((BN)_x(G2)_{1-x}\) are different, depending on whether the salts containing only \(G2\) are superconducting \((G2 = NB, BB)\) or not \((G2 = CB, DCB)\). As shown in Fig. 6, dielectric behavior before the superconducting transition appears clearly for the former (salts VIII, XI), while for the latter (VII, X) \(R(T)\) behaviour has a more pronounced metallic character, although they also undergo a transition to a superconducting state.

\(T_c\) for the monoclinic crystals with mixed solvents is dependent on the degree of substitution of the BN molecules by the molecules of the other guest, G2. If \(G2\) is 1,2-DCB (14%) or NB (20%) (VII and VIII, Table 1), \(T_c\) (7.2 \(K\) and 6.6 \(K\), respectively) changes insignificantly as compared with \(T_c\) for the crystals comprising BN only. The substitution of the BN molecules by FB (60%) or CB (65%) molecules (IX and X, Table 1) results in a further relatively small decrease of \(T_c\) (down to 6 \(K\)). In crystals of XI, where 83% of the BN molecules are substituted by the BB ones, a superconducting transition is observed below 4.2 \(K\) (the inset in Fig. 6). The transition was registered by measurement of the ac susceptibility, which clearly demonstrated the bulk character of the superconductivity in the sample. The conducting behaviour of the crystals of XI is similar to that of the crystals containing BB only (Fig. 6), i.e. the conductivity is determined mainly by the presence of the guest molecule \(G2\) when most of BN molecules have been substituted by G2 ones. These data are in good agreement with the results obtained for the crystals containing \((BN)_x(Py)=_{1-x}\) mixtures,\(^{16}\) in which a superconducting transition is not observed when more then 65% of the BN molecules are substituted by pyridine ones (crystals with Pyr only are not superconducting). Analysis of our data and the results of previous work\(^{16}\) shows that \(T_c\) of mixed crystals does not depend on the nature of \(G2\) when the degree of substitution of the BN molecules is less than 65%. For example, the \(T_c\) for the crystals with \((BN)_{0.86}(DCB)_{0.14}\) (VII) and \((BN)_{0.9}(Py)_{0.1}\) lie close to 7 \(K\) and for the crystals with \((BN)_{0.35}(CB)_{0.65}\) (X) and \((BN)_{0.34}(Py)_{0.66}\) \(T_c = 6\) and 5.8 \(K\), respectively. At higher degrees of the benzonitrile substitution, the presence or lack of the superconducting transition depends on the \(G2\) nature only.

The temperature dependence of the resistivity of novel triclinic crystals of XII, which contain alternating \(\alpha\) and ‘pseudo-\(\kappa\)’ BEDT-TTF layers, has metallic character down to 1.5 \(K\) (Fig. 7).

The conducting properties of the two new orthorhombic phases (VIIa, VIIIa, Table 1) are similar to the known ones.\(^1,4\) The salts are semiconductors, as is a new radical cation salt, \(\alpha\)-BEDT-TTF\(_6\)[Fe(C\(_2\)O\(_4\))\(_3\)]X (XIII).

### Conclusion

A modified procedure for the electrocrystallization of layered molecular conductors and superconductors of the known (BEDT-TTF)\(_x\)A\(_y\)[M\(_{100}\)(C\(_2\)O\(_4\))\(_3\)]-G family with paramagnetic anions has been proposed. The procedure consists of using, as the electrocrystallization medium, mixtures of solvents \(G\), which are included in the composition of the resulting salts as neutral guest molecules, with 1,2,4-TCB (or 1,3-DBB) and 96% ethanol. The prepared crystals have unusual morphologies. Most of them grow as thick plates or parallelepipeds perpendicular to the conducting layers, while usually in the BEDT-TTF salts the conducting layers are parallel to the plate planes.

Using the modified procedure we prepared:

i) the crystals of five new superconducting salts of the monoclinic series, comprising two guest solvents in the structure, \(\beta''\)-(BEDT-TTF)\(_4\)H\(_2\)O[Fe(C\(_2\)O\(_4\))\(_3\)]-(G1)\(_x\)(G2)\(_{1-x}\), where G1 is BN and G2 is FB, CB, 1,2-DCB, BB or NB;

ii) the crystals of two new semiconductors of the orthorhombic series, ‘pseudo-\(\kappa\)’-(BEDT-TTF)\(_4\)H\(_2\)O[Fe(C\(_2\)O\(_4\))\(_3\)]-(BN)\(_x\)(G2)\(_{1-x}\), where G2 is 1,2-DCB or NB;

iii) the crystals of the novel triclinic phase, \(\alpha\)-‘pseudo-\(\kappa\)’-(BEDT-TTF)\(_4\)H\(_2\)O[Fe(C\(_2\)O\(_4\))\(_3\)]-(1,2-DBB). This is the first radical cation salt in which conducting layers composed of BEDT-TTF molecules with \(\alpha\) and ‘pseudo-\(\kappa\)’ packing motif alternate. The difference in the BEDT-TTF layers is a result of an asymmetric arrangement of the guest solvent molecules in the anion layer with respect to the neighbouring \(\alpha\) and ‘pseudo-\(\kappa\)’ layers. The crystals have stable metallic properties down to 1.5 \(K\).
The crystals of two polymorphic modifications, $\beta''$ and ‘pseudo-κ’, which are superconductors and semiconductors, respectively, appeared in the same reactions: VII and VIIa, VIII and VIIIa (Table 1). However, it should be noted that highly conducting monoclinic $\beta''$ crystals dominate among the products of the modified electrochemical syntheses.

The G1 : G2 ratios in the structures of the monoclinic and orthorhombic crystals were refined from the single-crystal X-ray data. The ratios were distinct from the molar ratios of the solvents in the syntheses (Table 1). For the first time, positional disorder of both the hydroxonium cations and the solvent molecules in the anion layer was characterized in detail.

The conducting properties of the monoclinic crystals with mixed solvents (G1)$_x$(G2)$_{1-x}$ (VII–XI) are dependent on the degree of substitution of the BN molecules (G1) by molecules of another guest (G2). If a small amount of BN is replaced by 1,2-DCB (14%) or NB (20%), $T_C$ changes insignificantly (7.2 K and 6.6 K, respectively), as compared with $T_C$ for the crystals comprising BN only (7.4 K). The greater substitution of BN by FB (60%) or CB (65%) results in a further relatively small decrease of $T_C$ (6 K), while in the crystals where 83% of BN molecules are replaced by BB molecules, a superconducting transition is observed below 4.2 K.

Acknowledgements

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