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Organic conductors and superconductors based on bis(ethylenedithio)tetrathiafulvalene radical cation salts with supramolecular tris(oxalato)metallate anions

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The results of studies of a family of conductors and superconductors based on bis(ethylenedithio)tetrathiafulvalene radical cation salts with paramagnetic and diamagnetic supramolecular tris(oxalato)metallate anions are collated and analyzed. Methods for the preparation of these salts and various types of packing of conducting layers within the salt structures are considered. The transport properties of crystals of the salts of this family and the effect of guest solvent molecules on these properties are discussed. The contribution of scientists from the Institute of Problems of Chemical Physics, RAS, to the research into organic conductors and superconductors is noted.
The bibliography includes 70 references.

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I. Introduction

In the last 40 years, a new research area, associated with the synthesis and study of low-dimensional organic molecular conductors and superconductors, has formed. Researchers from the Institute of the Problems of Chemical Physics, Russian Academy of Sciences, have made a fundamental contribution to the development of this area. The problem of low-dimensional organic electrically conducting compounds appeared in relation to the well-known theoretical paper by Little,[1] an American physicist, who proposed in 1964 the exciton mechanism of superconductivity and invented a hypothetical one-dimensional polymeric molecule in which this mechanism could be implemented, resulting in a high critical superconducting transition temperature (T_c).[2] Although Little's reasoning and calculations were not sufficiently strict, his work attracted a lot of attention of physicists and chemists. This is understandable, because the traditional trend related to the development of superconducting alloys had largely run its course by that time. The critical superconducting transition temperature, which reached 18 K, had not increased for 15 years, despite considerable effort of physicists and metallurgical and materials scientists. Furthermore, some theoretical papers of that time stated that the phonon mechanism, which operates in traditional superconductors, cannot in principle provide T_c above 30 – 40 K. Therefore, the publication of Little, who proposed synthesizing a molecule with $T_c = 2000$ K,† could not, of course, go unnoticed.

The research aimed at the development of organic superconductors started in several countries (USA, Japan, France, Germany). Also, this work was initiated in Chernogolovka (USSR). In 1966, I.F.Shchegolev, a follower of P.L.Kapitsa, gathered a team of chemists, physicists and crystallographers at the Branch of the Moscow Institute of

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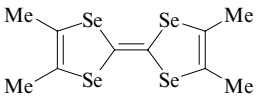
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Chemical Physics in Chernololovka [later, the Institute of Problems of Chemical Physics of the RAS (IPCP RAS)] and set them the task of creating organic superconductors. Moreover, not only superconductors, but even organic metals did not exist at that time, the mere problem of possible states in low-dimensional electronic systems was not at all clear. The first issue was to choose the investigation objects. I.V.Shchegolev immediately decided in favour of conducting molecular crystals rather than conducting polymers. He expected that the search for organic superconductors would be long and could be a success only with consistent structure – property analysis. Now it is clear that this research strategy has fully justified itself. Organic superconductors were indeed discovered in the early 1980s among molecular crystals, whereas polymeric organic superconductors have not yet been obtained.

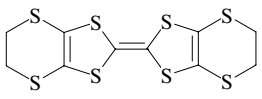
The 'organic' superconductivity was found among electrically conducting quasi-one-dimensional radical cation salts based on a selenium-containing π-donor, tetramethyltetraselenafulvalene [TMTSeF (**I**)]. The superconductivity was first established at a pressure of ~11 kbar for the salt $(TMTSeF)_2PF_6$ (Ref. 3) and then in the TMTSeF perchlorate at ambient pressure.[4] The studies of TMTSeF salts provided a lot of new data that were of interest for solid-state physics; however, this line of research was not very promising for extending the number of organic superconductors and increasing T_c. Seven superconductors were found among TMTSeF salts, but only one of them $[(TMTSeF)_2ClO_4]$ switched to the superconducting state at an ambient pressure. All superconducting TMTSeF salts contain octahedral (PF_6, AsF_6, SbF_6, TaF_6) or tetrahedral (ClO_4 , ReO_4, FSO_3) anions, are isostructural, and have low T_c (about 0.9 – 2.0 K).[5,6]

The discovery of superconductivity in TMTSeF salts triggered the search for organic superconductors based on radical cation salts of other π-donors with tetrahedral or octahedral anions. Soon this resulted in the synthesis of the first superconductor based on bis(ethylenedithio)tetrathiafulvalene [BEDT-TTF (**II**)] — the radical cation salt $(BEDT\text{-}TTF)_2ReO_4$, which switched to the superconducting state at a pressure of 6 kbar and $T_c \approx 2$ K.[7] In the structure and physical properties, this salt resembles quasi-one-dimensional superconductors of the TMTSeF family.[8]

Structures I, II



I



II

The next fundamental step towards 'organic' superconductivity was made at the IPCP RAS: in 1983, the first quasi-two-dimensional organic superconductor, bis(ethylenedithio)tetrathiafulvalene triiodide, with $T_c = 1.4$ K at ambient pressure was synthesized[9,10] (see‡). In a little while, it was found that at a moderate pressure (~0.5 kbar), a new superconducting state with $T_c = 8$ K appears in the $(BEDT\text{-}TTF)_2I_3$ crystals.[11,12] Later on, the phase with $T_c = 8$ K was stabilized at an ambient pressure[13] and was shown to be fully ordered, unlike the phase with $T_c = 1.4$ K, the structure of which has a disorder in the arrangement of terminal $CH_2 - CH_2$ groups of the BEDT-TTF molecule.[14] The 18-year (from 1966 to 1984) quest of researchers from the IPCP RAS for organic superconductors is reflected in the review of Yagubskii.[15]

The discovery of quasi-two-dimensional organic superconductors, which immediately provided a several-fold increase in T_c compared with the T_c values of TMTSeF-based superconductors, had a pronounced effect on the search for organic superconductors and resulted in the vigorous development of the BEDT-TTF chemistry;[16] numerous salts based on BEDT-TTF and its derivatives with various types of anions have been prepared. To date, the number of organic superconductors of the BEDT-TTF family is more than a hundred and their T_c has increased to 12.5 K.[8,17–19]

Regarding the type of the crystal and electronic structure and some properties (low concentration of charge carriers, mixed oxidation state, high upper critical fields, presumed d-coupling), quasi-two-dimensional organic superconductors are close to high-temperature metal oxide superconductors and are considered as model objects for the study of superconductivity mechanism. It is also noteworthy that the search for organic superconductivity gave rise to a new class of low-dimensional solids, studies of which provided quite a number of important data for various topics of solid-state physics such as metal/dielectric and metal/superconductor transitions, coexistence of superconducting and dielectric transitions, charge and spin density waves, magnetic field-induced phase transitions, quantum spin liquid state, giant quantum and semiclassical oscillations of magnetoresistance and so on.[20]

The research concerned with the molecular design of organic superconductors is in progress. For a long period of time, the interest in the radical ion salts was associated with the organic superconductivity problem, but in the mid-1990s a new trend was initiated and started to develop, in particular, creation of bifunctional materials on the basis of radical ion salts combining the conductivity and magnetism in the same crystal lattic. The conductivity of these materials is provided by the organic radical cation subsystem, while the magnetism comes from the anion subsystem comprising paramagnetic transition metal ions. The combination of conductivity and magnetism in the crystals of radical cation salts and the synergism of these two properties can bring about new physical phenomena and new applications in molecular electronics.

Currently, molecular metals and superconductors with localized magnetic moments, antiferromagnetic metals and superconductors, and ferromagnetic molecular metals have been synthesized on the basis of radical cation salts.[21–25] In some of these salts, π – d-interaction was found between the conducting and magnetic subsystems; therefore, their conductivity can be controlled by varying the external magnetic field.[21,26–29] Compounds of this type may form a basis for the development of molecular spintronics.

Among the radical cation salts with paramagnetic metal complex anions, most numerous and diverse in the structure and conductivity is the family of BEDT-TTF salts with tris(oxalato)metallate anions $(BEDT\text{-}TTF)_4A^+[M^{3+}(C_2O_4)_3]\cdot G$, where $M^{3+} = Cr^{3+}$, Fe^{3+}, Mn^{3+}, Ru^{3+}; $A^+ = K^+$, Rb^+, NH_4^+,

‡ The paper[9] that initiated the research into the quasi-two-dimensional organic superconductors is a part of the *JETP Letters* Golden Archive, which includes publications with the highest citation indexes since the foundation of the journal.

H_3O^+; G is the so-called guest solvent molecule (a neutral molecule). A distinctive feature of this salt family is the supramolecular nature of their counter-ions, which contain a guest solvent molecule (according to the host–guest type).

The nature, size and shape of the guest molecule considerably affect the structure and conductivity of these compounds. Researchers from the IPCP RAS, together with specialists from the Institute of Solid State Physics in Chernogolovka made a large contribution to the synthesis and research into the structure and conducting properties of this family. These issues are covered in the present review.

II. Radical cation salts of BEDT-TTF with supramolecular tris(oxalato)metallate anions

The first molecular paramagnetic superconductor, (BEDT-TTF)$_4$A$^+$[M^{3+}(C$_2$O$_4$)$_3$]·G (A$^+$ = H_3O^+; M^{3+} = Fe^{3+}, G = PhCN) with T_c = 7–8.5 K, was synthesized in 1995.[30] Then by varying the A, M and G components, an extensive family of BEDT-TTF radical cation salts with paramagnetic and non-magnetic tris(oxalato)metallate anions (M^{3+} = Cr^{3+}, Fe^{3+}, Mn^{3+}, Ru^{3+}, Ga^{3+}, Al^{3+}, Co^{3+}; A$^+$ = H_3O^+, K$^+$, NH_4^+, Rb$^+$; G is a neutral molecule) was synthesized.[31–51] In the crystals of this family, the conducting radical cation layers alternate with two-dimensional anionic layers with a honeycomb-like structure: the M^{3+} and A$^+$ cations linked by oxalate bridges form hexagonal cavities, which are able to incorporate neutral solvent molecules (Fig. 1).

The anionic layers do not directly participate in the conductivity, but the shape, size and chemical nature of the anions determine the number and geometry of the cation–anion contacts, which dictate the type of packing of BEDT-TTF molecules and, hence, the conducting properties of the crystals. With the same π-donor (BEDT-TTF) and various anions, crystals with different types of packing of radical cation layers have been obtained. Also, crystals with different types of packing can be prepared with the same anion by varying the conditions of synthesis, because the differences between the packing energies of BEDT-TTF radical cations are small. The degrees of influence of components of the supramolecular anionic layer {A$^+$[M^{3+}(C$_2$O$_4$)$_3$]·G}$^{2-}$ on the structure and properties of the resulting crystals are different.

The principal factors that determine the structure and properties of the given family of crystals are the size, shape and chemical nature of guest solvent molecules G. The other two components of the anionic layer (M^{3+} and A$^+$ cations) affect the properties to a much lesser extent: the variation of M^{3+} with the same G does affect T_c, whereas the nature of the singly charged A$^+$ cation barely affects the properties of the crystals.

In terms of the symmetry type, three groups of (BEDT-TTF)$_4$A$^+$[M^{3+}(C$_2$O$_4$)$_3$]·G crystals can be distinguished: monoclinic, orthorhombic and triclinic. The crystals have the same stoichiometric composition but different types of conducting layers packing: *β″*, *pseudo-κ*, *α–pseudo-κ* and *α–β″* (Fig. 2), according to the structural classification of the salts of BEDT-TTF and its analogues.[31, 32]

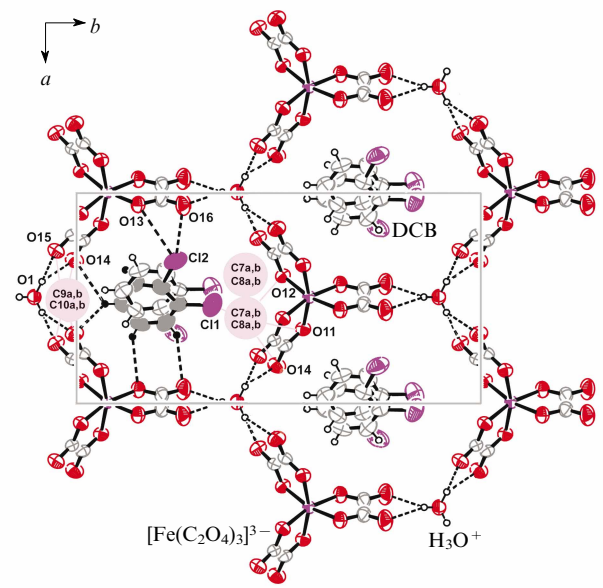


Figure 1. Supramolecular anionic layer {A$^+$[M^{3+}(C$_2$O$_4$)$_3$]·G}$^{2-}$ (Ref. 45).
G is a 1,2-dichlorobenzene (DCB) molecule; M^{3+} = Fe^{3+}; A$^+$ = H_3O^+

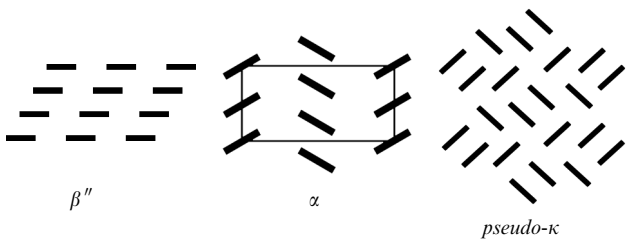


Figure 2. Schematic view of the types of packing of BEDT-TTF molecules in the (BEDT-TTF)$_4$A$^+$[M^{3+}(C$_2$O$_4$)$_3$]·G crystals.
View along the long axis of the BEDT-TTF molecule.

The organic layer in the *β″* crystals is composed of stacks of the BEDT-TTF radical cations, the planes of which are almost parallel and shifted with respect to the short axis. The angle between the molecular plane and the stack axis is ~60°. In the α-phases, the stacks are inclined to one another. In the crystals with a *pseudo-κ* type of packing, the organic layer is formed by charged [(BEDT-TTF)$_2$]$^{2+}$ dimers surrounded by neutral [BEDT-TTF]^0 molecules, which are perpendicular to the dimers.

The monoclinic crystals (space group *C*/2c) with the *β″* packing type of the BEDT-TTF molecules possess the most interesting properties. All superconducting phases belong to this group; in some of them, structural phase transitions take place on lowering the temperature. Monoclinic crystals were prepared for a large number of chemically different guest solvents.[30, 33–51]

The group of orthorhombic crystals (space group *Pbcn*) with *pseudo-κ*-packing type of conducting layers includes several semiconducting radical cation salts (M^{3+} = Fe^{3+}, Cr^{3+}, Co^{3+}, Al^{3+}; A$^+$ = K$^+$, NH_4^+, H_3O^+; G = PhCN and its mixtures with $PhNO_2$ or 1,2-$Cl_2C_6H_4$).[30, 34, 44]

Triclinic crystals (space group $P\bar{1}$) are formed with large unsymmetrical (including chiral) solvent molecules [M^{3+} = Fe^{3+}, G = PhAc, (*X*)-PhCH(OH)Me, *X* = *R*/*S* (racemate) or *S* (enantiomer), 1,2-$Br_2C_6H_4$; M^{3+} = Ga^{3+},

G = PhN(Me)CHO, BnCN, 1,2-$Br_2C_6H_4$].[44, 46, 47, 52, 53] Their structures are composed of alternating conducting layers with two types of packing, α and β'' or α and *pseudo*-κ.

III. Synthesis of the $(BEDT\text{-}TTF)_4A[M(C_2O_4)_3]\cdot G$ crystals

All crystals of the $(BEDT\text{-}TTF)_4A^+[M^{3+}(C_2O_4)_3]\cdot G$ family were obtained by the electrochemical oxidation of BEDT-TTF at a platinum electrode in organic solvents in the presence of electrolytes, namely, ammonium or potassium tris(oxalato)metallates combined with a crown ether. The reaction medium for the crystal growth consists of the guest solvent either neat or mixed with other solvents, which are not incorporated in the structure but have a considerable effect on the electrocrystallization, in particular, they increase the solubility of the inorganic electrolyte in the guest organic solvent and, hence, enable variation of the current and the donor/electrolyte molar ratio, *i.e.*, parameters that largely determine the crystal structure, growth rate and quality.

III.1. Electrochemical oxidation of BEDT-TTF in the guest solvent with small amounts of H_2O, MeOH or H_2O – MeOH

The 'parents' of the given family of crystals are radical cation salts incorporating PhCN: two monoclinic superconducting salts with the β'' type of packing of the BEDT-TTF molecules ($M^{3+} = Fe^{3+}$ or Cr^{3+}, $A^+ = H_3O^+$; T_c = 7.0 – 8.5 and 6 K, respectively) and two semiconducting salts of the orthorhombic series ($M^{3+} = Fe^{3+}$, $A^+ = K^+$ or NH_4^+) with the *pseudo*-κ packing of the conducting layer.[30, 33, 34] A specific feature of the electrochemical synthesis of the crystals of these salts is that semiconducting crystals grow in anhydrous PhCN, while using PhCN with small amounts of water added gives rise to superconducting monoclinic crystals along with orthorhombic ones. The superconducting monoclinic crystals contain H_3O^+ as the A^+ cations, whereas semiconducting crystals contain NH_4^+ or K^+ cations.

The superconducting crystals grow as needles. Because of the poor quality of the crystals, researchers[30] were unable to locate the hydroxonium cation in the structure; instead, they placed an H_2O molecule into the crystal. Subsequently, the presence of hydroxonium cations in the monoclinic crystals was demonstrated unambiguously by IR spectroscopy and X-ray diffraction. It is also noteworthy that the synthesis of these superconducting crystals is poorly reproducible; most often, only semiconducting crystals are formed. Evidently, this is related to the separation of the water – organic mixture into layers during the synthesis; as a result, most of the electrolyte migrates from the organic layer into the thin aqueous layer (film) on the solvent surface, thus creating conditions for the growth of the semiconducting phase in the 'dehydrated' organic medium.

In the subsequent years, monoclinic crystals with $M^{3+} = Fe^{3+}$, Cr^{3+}, Ga^{3+}, Mn^{3+} and Ru^{3+} containing molecules of various guest solvents, G = PhX (X = NO_2, Cl, F, Br), DMF, CH_2Cl_2, 1,2-$Cl_2C_6H_4$, Py or HalPy, were prepared.[30, 33 – 51] The crystals were formed in pure guest solvents, guest solvents G with small amounts of water and mixtures of G with methanol, ethanol and other solvents that are not incorporated in the crystal structure (Table 1 – 3).

Table 1. Conducting properties of the monoclinic radical cation salts (space group *C*2/*c*) $(BEDT\text{-}TTF)_4H_3O[M(C_2O_4)_3]\cdot G$ with β'' type of packing obtained in G + H_2O and/or MeOH.

Salt	G	M^{3+}	Conducting properties	Ref.
1	PhCN	Fe^{3+}	Superconductor, T_c = 7.0 – 8.5 K	30
2	PhCN	Cr^{3+}	Superconductor, T_c = 5.5 – 6.0 K	33, 34
3	$PhNO_2$	Fe^{3+}	Superconductor, T_c = 6.2 K	35
4	$PhNO_2$	Cr^{3+}	Superconductor, T_c = 5.8 K	35
5[a]	$PhNO_2$	Ga^{3+}	Superconductor, T_c = 7.5 K	36
6[a]	PhBr	Fe^{3+}	Superconductor, T_c = 4 K	37 – 39
7	PhBr	Cr^{3+}	Superconductor, T_c = 1.5 K	38, 39
8	PhBr	Mn^{3+}	Superconductor, T_c = 2 K	39
9	PhF	Fe^{3+}	Superconductor, T_c < 1 K	38, 39
10	PhCl	Fe^{3+}	Metal, T > 0.4 K	38 – 40
11	PhCl	Cr^{3+}	Metal, T > 130 K	38
12	Py	Fe^{3+} (A = Rb^+, H_3O^+)	Metal, T > 0.5 K	40 – 42
13	Py	Cr^{3+}	The same	42
14	Py	Ga^{3+}	Superconductor, T_c < 2 K	36

[a] Crystals were obtained without adding H_2O and/or MeOH.

Crystals **5** and **6** (see Table 1, G = $PhNO_2$ and PhBr, respectively) were obtained in guest solvents, while in other cases, some water or H_2O – MeOH mixture was added to the reaction medium.[38] In a later publication,[39] crystals with G = PhX (X = Cl, Br, F) were prepared in PhX + MeOH mixtures. The crystals contained H_3O^+ cations and this provided grounds for assuming that the guest solvents used in the synthesis of these crystals (and also crystals **5** and **6**) contained traces of water. The crystals obtained with these solvents were of different quality. For example, crystals with G = $PhNO_2$ ($M^{3+} = Fe^{3+}$, Cr^{3+}) grew as small thin plates. Also, crystals with $M^{3+} = Fe^{3+}$ often formed as twins. Unlike crystals with $PhNO_2$, crystals with PhBr ($M^{3+} = Fe^{3+}$) were obtained as rectangular prisms with a square cross-section and served as convenient objects for physical investigations.[37]

III.2. Electrochemical oxidation of BEDT-TTF in mixtures of several solvents

Monoclinic crystals with dichloromethane, in which the electrolyte and BEDT-TTF are poorly soluble, were obtained using its mixtures with acetonitrile and 2-chloropyridine as the reaction medium.[40, 43] The two latter components did not enter the crystal structure, but they were necessary, because a small quantity of very thin single

Table 2. Structural and conducting properties of the radical cation salts (BEDT-TTF)$_4$H$_3$O[M(C$_2$O$_4$)$_3$]·G obtained in guest solvents G in the presence of 1,2,4-trichlorobenzene and/or 95% ethanol.

Salt	G (see [a])	M^{3+}	Symmetry	Type of packing	Conducting properties	Ref.
15	$(PhCN)_{0.17}(PhBr)_{0.83}$	Fe^{3+}	*C*2/*c*	*β″*	Superconductor, T_c = 4.2 K	44
16	$(PhCN)_{0.86}(1,2\text{-}Cl_2C_6H_4)_{0.14}$	Fe^{3+}	*C*2/*c*	*β″*	Superconductor, T_c = 7.2 K	44
17	$(PhCN)_{0.88}(1,2\text{-}Cl_2C_6H_4)_{0.12}$	Fe^{3+}	*Pbcn*	*pseudo*-κ	Semiconductor	44
18	$(PhCN)_{0.8}(PhNO_2)_{0.2}$	Fe^{3+}	*C*2/*c*	*β″*	Superconductor, T_c = 6.6 K	44
19	$(PhCN)_{0.8}(PhNO_2)_{0.2}$	Fe^{3+}	*Pbcn*	*pseudo*-κ	Semiconductor	44
20	$(PhCN)_{0.40}(PhF)_{0.60}$	Fe^{3+}	*C*2/*c*	*β″*	Superconductor, T_c = 6.0 K	44
21	$(PhCN)_{0.35}(PhCl)_{0.65}$	Fe^{3+}	*C*2/*c*	*β″*	The same	44
22	$1,2\text{-}Cl_2C_6H_4$	Fe^{3+}	*C*2/*c*	*β″*	Metal, T > 0.4 K	45
23	$1,2\text{-}Br_2C_6H_4$	Fe^{3+}	$P\bar{1}$	α – *pseudo*-κ	The same	44, 46
24	$1,2\text{-}Br_2C_6H_4$	Ga^{3+}	$P\bar{1}$	α – *pseudo*-κ	"	47
25	PhBr	Ga^{3+}	*C*2/*c*	*β″*	"	47
26	PhBr	Ru^{3+}	*C*2/*c*	*β″*	Superconductor, T_c = 6.3 K	48
27	2-ClPy	Fe^{3+}	*C*2/*c*	*β″*	Superconductor, T_c = 2.4 – 4.0 K	49
28	2-BrPy	Fe^{3+}	*C*2/*c*	*β″*	Superconductor, T_c = 4.3 K	49
29	3-ClPy	Fe^{3+}	*C*2/*c*	*β″*	Metal, T > 0.4 K	49
30	3-BrPy	Fe^{3+}	*C*2/*c*	*β″*	The same	49

[a] Molar ratio of the guest solvents in the structure (according to X-ray diffraction data).

Table 3. Structural and conducting properties of the radical cation salts (BEDT-TTF)A[M(C$_2$O$_4$)$_3$]·G obtained in guest solvents G.

Salt	G	M^{3+}	A^+	Symmetry	Type of packing	Conducting properties	Ref.
31	DMF	Fe^{3+}	NH_4^+	*C*2/*c*	*β″*	Superconductor, T_c < 2 K	50, 51
32	DMF	Cr^{3+}	NH_4^+	*C*2/*c*	*β″*	Metal, T > 4.2 K	50, 51
33	DMF	Cr^{3+}	$[K_x(NH_4)_{1-x}]^+$	*C*2/*c*	*β″*	The same	50, 51
34	DMF	Cr^{3+}	K^+	*C*2/*c*	*β″*	"	50, 51
35	PhN(Me)COH	Ga^{3+}	NH_4^+	$P\bar{1}$	α – *β″*	Semiconductor	52
36	BnCN	Ga^{3+}	NH_4^+	$P\bar{1}$	α – *β″*	"	52
37	PhAc	Fe^{3+}	NH_4^+	$P\bar{1}$	α – *β″*	"	52
38	(*X*) – PhCH(OH)Me *X* = *R*/*S* or *S*	Fe^{3+}	NH_4^+	$P\bar{1}$	α – *β″*	Semiconductor (*X* = *R*/*S*); metal – semiconductor (*X* = *S*)	53

crystals with G = CH_2Cl_2 was formed only in their presence. In a mixture containing no 2-chloropyridine, the preparation of crystals failed.

In order to extend the number of crystals of this family with guest solvents in which electrolytes and BEDT-TTF are poorly soluble, a procedure has been developed [44] for crystal preparation in a mixture of one or two guest solvents G1 – G2 with 1,2,4-trichlorobenzene (or 1,3-dibromobenzene) and/or 96% EtOH, which were not present in the structure but played an important role in the electrochemical synthesis. An advantage of adding 96% EtOH over the addition of H_2O or a MeOH – H_2O mixture is the formation of a more stable emulsion. This is important because electrocrystallization may last for several weeks. The presence of 1,2,4-trichlorobenzene (or 1,3-dibromobenzene) in the reaction medium facilitates the formation of high-quality monoclinic crystals, including the crystals with PhCN (Fig. 3).

This procedure was employed to prepare monoclinic crystals containing 1,2-dichlorobenzene, various isomers of monohalopyridines HalPy (Hal = Cl, Br), a series of radical cation salts containing a mixture of two solvents $(G1)_x(G2)_{1-x}$, where G1 = PhCN, G2 = PhF, PhCl, PhBr, $PhNO_2$ or $1,2\text{-}Cl_2C_6H_4$, and superconducting crystals containing a 4d metal cation (M^{3+} = Ru^{3+}, G = PhBr) (see Table 2).

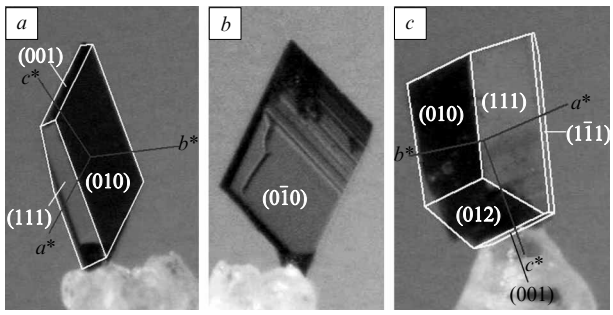


Figure 3. Photographic images of crystals **1** (G = PhCN) and **20** [G = $(PhCN)_{0.40}(PhF)_{0.60}$] taken during the X-ray experiment; one can see the unusual crystal morphology: the *b** axis along which the BEDT-TTF layers run is perpendicular to the plate plane.[44]
(*a*) Orientation of the axes and designation of faces for crystal **1**; (*b*) growth stripes on the (0$\bar{1}$0) surface of crystal **1**; (*c*) orientation of the axes and face indices for crystal **20**.

It should be noted that the quality of monoclinic crystals obtained by this procedure was sufficient for locating the hydroxonium cations in the structure by X-ray diffraction.[44] The use of 1,2-dibromobenzene as the guest solvent with addition of 96% EtOH resulted in triclinic crystals **23** and **24** (see Table 2) possessing stable metallic properties down to liquid helium temperatures. Two types of conducting layers alternate in the structure of these crystals, namely, α and *pseudo*-κ.[44, 46, 47]

This procedure made it possible to increase not only the crystal quality but also the selectivity of electrocrystallization: crystals of orthorhombic semiconducting phases **17** and **19** (see Table 2), which usually accompany the monoclinic crystals, were detected only in two syntheses and only in minor amounts. An unusual morphology of the crystals obtained in the presence of 1,2,4-trichlorobenzene or 1,3-dibromobenzene deserves attention. The crystals grew as thick plates or prisms (see Fig. 3) and, unlike most of crystals of BEDT-TTF salts in which the conducting layers are arranged in the plate plane, in these crystals conducting layers were perpendicular to this plane.

III.3. Electrochemical oxidation of BEDT-TTF in the medium of guest solvents

Several monoclinic and triclinic crystals of the $(BEDT\text{-}TTF)_4A^+[M^{3+}(C_2O_4)_3]\cdot G$ family were prepared in guest solvents without any other solvents added. These are monoclinic crystals incorporating *N,N*-dimethylformamide molecules,[50, 51] and triclinic $\alpha-\beta''$ crystals in which G = PhAc, (*X*)-PhCH(OH)Me, PhN(Me)CHO or BnCN.[52, 53] In these crystals, A^+ is either an ammoinum or a potassium cation, like the orthorhombic phases (see Table 3). Good quality of the crystals obtained in DMF is also noteworthy; in our opinion, this is attributable to high solubility of electrolytes in DMF. In particular, crystals **31** (see Table 3) were prepared without adding crown ether, which was necessary in all other cases.

III.4. Ability of molecules of various solvents to be incorporated in the anionic layer

For crystals **15** – **21** (see Table 2) containing two guest solvents, it was found that the ratio of the solvents in the crystal structure is determined by the nature of G2 rather than the G1 to G2 ratio in the reaction medium. For example, when the reaction medium comprises an equimolar PhCN – PhCl mixture, crystals **21** containing 35% PhCN and 65% PhCl are formed (see Table 2). Similar crystals are formed with a twofold molar excess of PhCl in the reaction medium. If PhCN and PhF are present in equal molar amounts, the resulting crystals **20** contain 40% PhCN and 60% PhF. A twofold molar excess of PhCN with respect to PhBr results in the formation of crystals **15** containing 83% of PhBr. The fractions of $PhNO_2$ and $1,2\text{-}Cl_2C_6H_4$ in the structures of crystals **18** and **16** with respect to PhCN are 20% and 14%, respectively, in the case of equimolar ratio of the solvents in the reaction mixture.

In terms of the ability to be incorporated into monoclinic crystals, the considered guest solvents can be arranged in the sequence

$$1,2\text{-}Cl_2C_6H_4 < PhNO_2 < PhCN < PhF < PhCl < PhBr$$

This result is correlated with the relative ease of the synthesis and high quality of crystals containing PhBr. It may also be noted that only with G = PhBr, superconducting monoclinic crystals containing Mn^{3+} and Ru^{3+} were formed. These crystals could not be prepared with other solvents.

IV. Structure of the $(BEDT\text{-}TTF)_4A[M(C_2O_4)_3]\cdot G$ crystals

In all of the crystals of the family in question, the conducting radical cation layers alternate along the *c* axis with layers of the $\{A^+[M^{3+}(C_2O_4)_3]^{3-}\cdot G\}^{2-}$ complex anions (Fig. 4). The structure of anionic layers in the crystals of different symmetry is nearly the same, whereas conducting layers are packed differently in the monoclinic, orthorhombic and triclinic crystals. Figure 4*a* shows the structure of monoclinic crystals in which the conducting layers with the β''packing type alternate with anionic layers.

In the orthorhombic crystals, the radical cation layers have a *pseudo*-κ type of packing. The triclinic crystals are composed of alternating conducting layers with two different types of packing: α and *pseudo*-κ or α and β'' (so-called bi-layered crystals, Fig. 4*b*). The bi-layered crystals are formed when the anionic layer contains bulky unsymmetrical solvent molecules, which are arranged unsymmetrically relative to neighbouring conducting layers and interact with them in different ways.[46, 47, 52, 53] The interaction within different layers and between the layers is provided by a multitude of interatomic contacts, which are shorter than the corresponding van der Waals radii.

IV.1. Structure of the conducting layers

A projection of a radical cation layer of monoclinic crystals ($G = 1,2\text{-}Cl_2C_6H_4$) is shown in Fig. 5. The conducting layer has a β'' type packing and consists of stacks, which run in different directions (along the [310] and [3$\bar{1}$0] axes, respectively) in neighbouring layers ($z = 0$ and $z = 0.5$).

The structure contains two crystallographically independent BEDT-TTF molecules (*I*, *II*), which are located in the stacks in the following sequence: *I*–*I*–*II*–*II*–*I*–*I* (Fig. 5). The ethylene groups in molecule *II* are ordered, whereas in molecule *I*, they are disordered over two sites. The bond lengths in both molecules are similar and correspond to the $(BEDT\text{-}TTF)^{0.5+}$ charge state. The planes of the central TTF moieties of the molecule are parallel within a layer and are arranged at an angle of $\sim 65^\circ$ relative to the TTF planes of neighbouring layers. The shortest and most numerous intermolecular contacts, S···S = 3.399 – 3.575(1) Å, are those between the stacks in the plane of the BEDT-TTF molecules. They are designated by the letters *A*, *F* and *H* in Fig. 5. One shortened contact, S···S = 3.667(1) Å, is present in the stack (contact *C*). The distances between the TTF planes of the neighbouring π-donors in the stack are 3.65(3), 3.63(3) and 3.534(5) Å (contacts *B*, *C* and *G*, respectively).

The orthorhombic crystals contain conducting layers with *pseudo*-κ packing type. The charge of the BEDT-TTF molecules in a *pseudo*-κ layer, unlike that in a β'' layer, is distributed non-uniformly: the layer is composed of charged $[(BEDT\text{-}TTF)_2]^{2+}$ dimers surrounded by neutral $(BEDT\text{-}TTF)^0$ molecules oriented perpendicular to the dimers (Fig. 6).

Because of strong charge localization on the dimers, this layer should behave as a semiconductor. This conclusion was confirmed by measurement of the temperature depend-

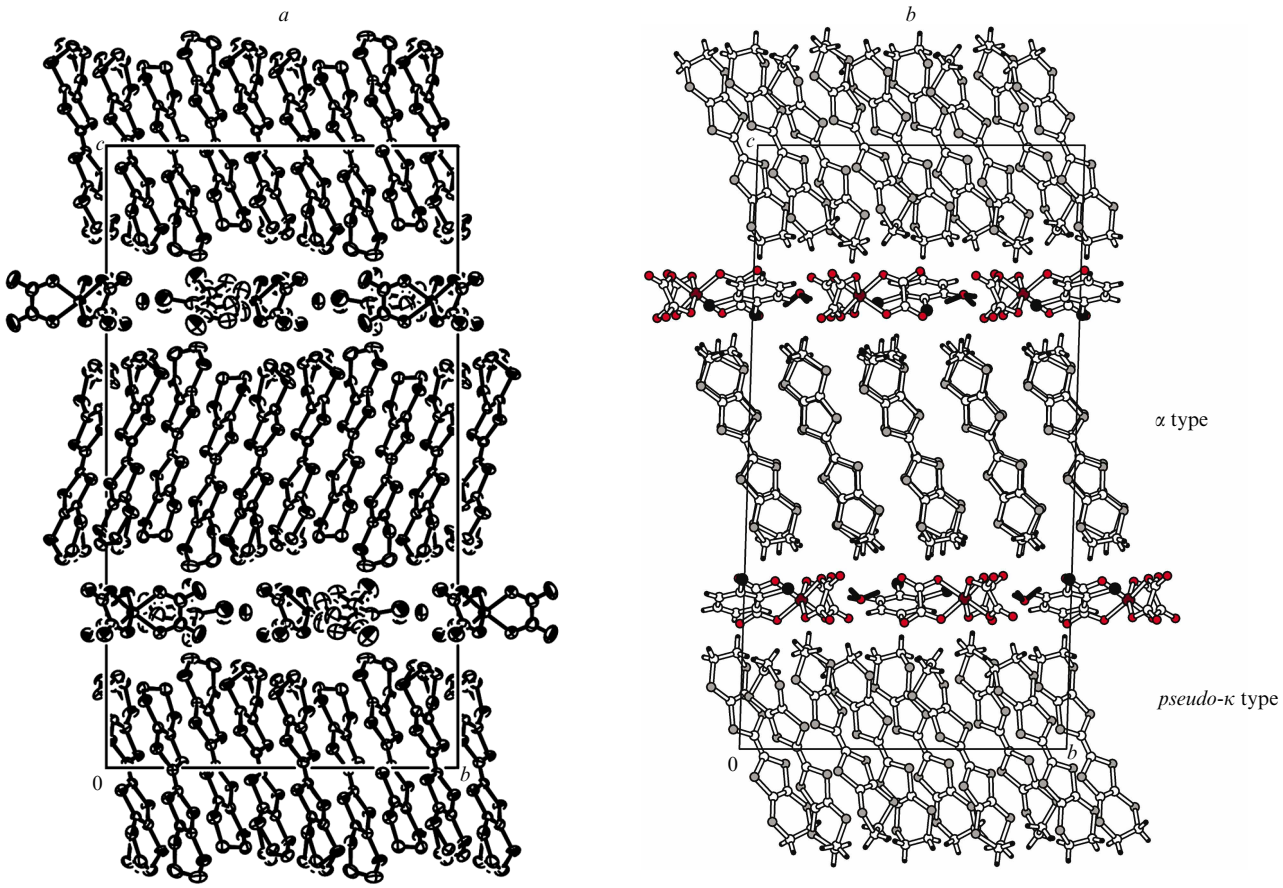


Figure 4. Structures of crystals **22** (projected along the *a* axis) (*a*)[45] and bi-layered crystals **23** composed of alternating conducting layers with different types of packing of radical cations (*b*).[46]

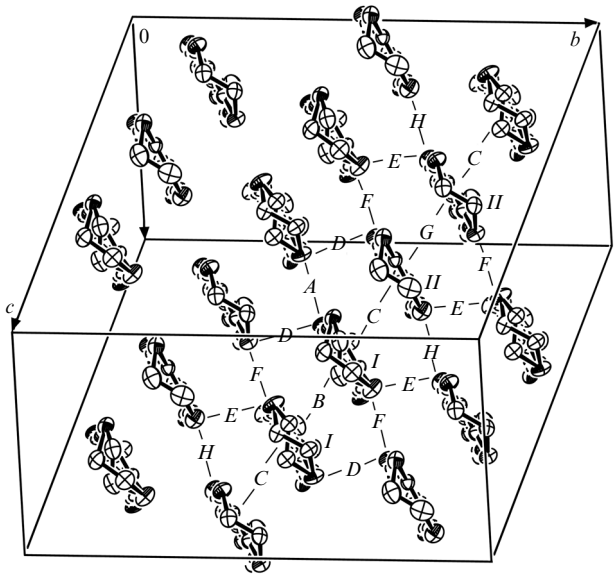


Figure 5. Radical cation layer ($z = 0.5$) in monoclinic crystals **22** (view along the long axis of the BEDT-TTF molecule).[45]
The numbers *I* and *II* designate two independent BEDT-TTF molecules and the letters denote the intermolecular contacts in a layer (see text).

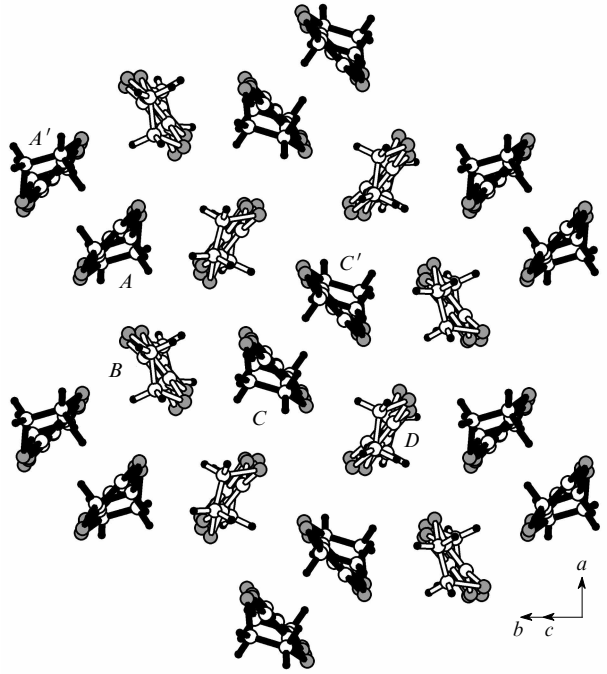


Figure 6. Radical cation *pseudo-κ* layer in bi-layered crystals **23**.[46]
$A-A'$, $C-C'$ are the charged $[(BEDT\text{-}TTF)_2]^{2+}$ dimers;
B, *D* are neutral $[BEDT\text{-}TTF]^0$ molecules.

ence of the electrical resistance of orthorhombic crystals and calculations of the electronic structure.[30, 44, 46]

Triclinic radical cation salts **35** – **38** were prepared by a UK and Japanese research team; the crystal and electronic structures of these salts were reported.[52, 53] Compounds **23** and **24** were prepared by the authors of this review. The quality of α – *pseudo*-κ crystals was sufficient for performing a detailed analysis of the crystal and electronic structures of the α-layers.[46, 47] The radical cation α-layer in the α – *pseudo*-κ crystals contains four crystallographically independent BEDT-TTF molecules (*E*, *H*, *F*, *G*), which form three independent BEDT-TTF stacks along the *a* direction (Fig. 7).

The molecular planes in the neighbouring stacks are located at angles of 92° – 97° relative to one another. Stacks *E* and *H* consist of identical molecules (*E* or *H*, respectively), whereas stack *FG* is composed of alternating molecules (*F* and *G*). All stacks are characterized by large and rather similar interplanar spacing between the neighbouring radical cations: 3.85(1) and 3.97(1) Å in stack *E*, 3.70(6) and 3.77(6) Å in stack *FG* and 3.72(1) and 3.86(1) Å in stack *H*. The large angle between the molecular planes and the stack axis (~45°) accounts for the virtually complete absence of intrastack overlap of the BEDT-TTF orbitals; overlapping orbitals are only those of sulfur atoms of the external six-membered rings of neighbouring π-donor molecules. All intermolecular S···S contacts within a stack are longer than the sum of the van der Waals radii, which is equal to 3.70 Å; meanwhile, there are numerous shortened S···S contacts in the 3.423(2) – 3.695(2) Å range between the stacks.

The terminal ethylene groups in molecule *E* occur in a staggered conformation, those of molecules *F* and *G* are in an eclipsed conformation, and in molecule *H*, the percentages of the eclipsed and staggered conformations are 65% and 35%, respectively, *i.e.*, one of ethylene groups is positionally disordered.

Analysis of the central C=C bond lengths in the BEDT-TTF molecules (*E*, *F*, *G*, *H*) demonstrated that the charge on each of the four radical cations in the α-layer is close to 0.5+. The regular structure and the equal charges of the radical cations of the α-layer suggest that this layer should possess metallic conduction. The calculations of the electronic band structure demonstrated that all intermolecular interactions in the α-layer (both within a stack and between stacks) are rather similar in magnitude, so that this layer can be considered as a two-dimensional metallic network formed by the interacting highest occupied molecular orbitals.[46]

IV.2. Structure of anionic layers

Unlike conducting layers, the anionic layers in crystals of different symmetry have approximately the same structure resembling honeycombs (Fig. 8). The three-component anionic layer, $\{A^+M^{3+}(C_2O_4)_3]^{3-}\cdot G\}^{2-}$, can be considered as a supramolecular assembly consisting of a host and a guest. The host is the hexagonal network the vertices of which are occupied by alternating M^{3+} and A^+ cations linked by oxalate bridges. The inner oxygen atoms of the C_2O_4 groups of the anion are octahedrally coordinated to the metal atom, while the external oxygen atoms are involved in hydrogen bonding with the A^+ cation (H_3O^+, K^+, NH_4^+). The guests, neutral solvent molecules, are located in the hexagonal cavities of the anionic layer (Fig. 8). The cavity sizes in the crystals of different symmetry are nearly equal. Analysis of the structure of the anionic layer in monoclinic crystals performed by Zorina *et al.*[45] demonstrated that the size of the hexagonal cavity virtually does not depend on the size of the guest solvent molecule, but is determined by the size of the M^{3+} cation and the distance from the external oxalate bridge oxygen atoms to the A^+ cation. Indeed, for the crystals with Fe^{3+} ions, the area of the cavity is 103 ± 1 Å^2, although the molecular volumes of the solvents differ by up to 40 – 50 Å^3.

Large unsymmetrical molecules of guest solvents [G = PhN(Me)COH, BnCN, PhAc, (*X*)-PhCH(OH)Me (*X* = *R*/*S* or *S*), 1,2-$Br_2C_6H_4$] are arranged in the cavity

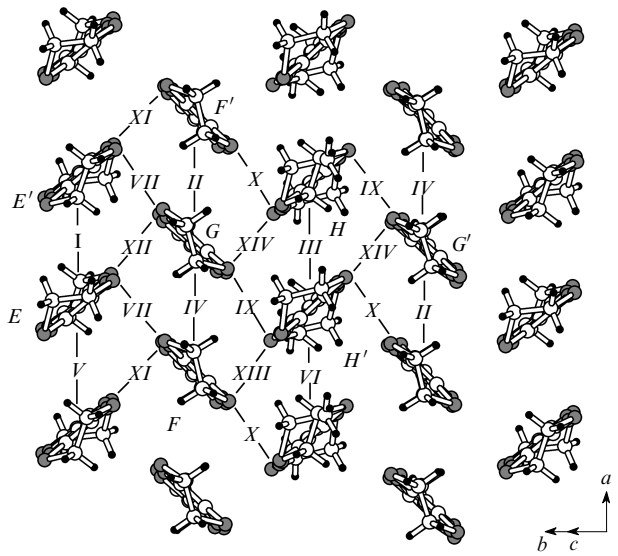


Figure 7. Radical cation α-layer in bi-layered crystals **23**.[46] The numbers *I* – *XIV* designate the intermolecular interactions in a layer; for interpretation of the letters, see text.

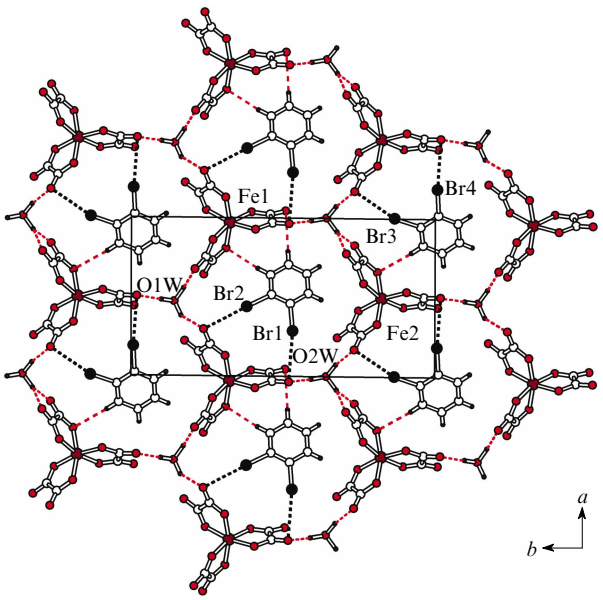


Figure 8. Complex anionic layer in bi-layered crystals **23**.[46]

unsymmetrically with respect to the neighbouring conducting layers and interact with them in different ways. Both bromine atoms of the 1,2-$Br_2C_6H_4$ molecule in the α–*pseudo*-κ-(BEDT-TTF)$_4H_3O[Fe(C_2O_4)_3]\cdot$1,2-$Br_2C_6H_4$ crystals point towards the α-layer and form three shortened C–H···Br hydrogen contacts with the terminal ethylene groups of radical cations *F* and *H*. The corresponding H···Br distances are 2.61, 2.78 and 2.82 Å. Hydrogen contacts of this type between the anionic and *pseudo*-κ layers are 2.98 Å. The hydroxonium cations are also arranged unsymmetrically relative to the α- and *pseudo*-κ-layers: all hydrogen atoms point towards the α-layer. Finally, the oxygen atoms of the tris(oxalato)metallate anion form numerous hydrogen bonds with the BEDT-TTF molecules of the α-layer (13 H···O bonds of 2.26–2.60 Å length), while only nine H···O bonds with length 2.37–2.57 Å are formed with the *pseudo*-κ layers. The unsymmetrical arrangement of components of the anionic layer relative to two neighbouring conducting layers has a crucial effect on packing of these layers and enables the coexistence in the crystal lattice of two conducting layers with different structure and charge distribution.

An unsymmetrical arrangement of anionic layer components is also present in the bi-layered crystals with the $\alpha-\beta''$ type of packing. In the salt crystals containing the chiral (*S*)-PhCH(OH)Me solvent, which exhibit the metal/semiconductor transition at 150–170 K, the solvent hydroxyl groups are located close to the α-layer surface, similar to the bromine atoms of the 1,2-$Br_2C_6H_4$ molecule in 'metallic' α–*pseudo*-κ crystals. Unlike this $\alpha-\beta''$ salt, in the semiconducting $\alpha-\beta''$ crystals, the polar CO and CN groups are located more closely to the β'' layer.[53]

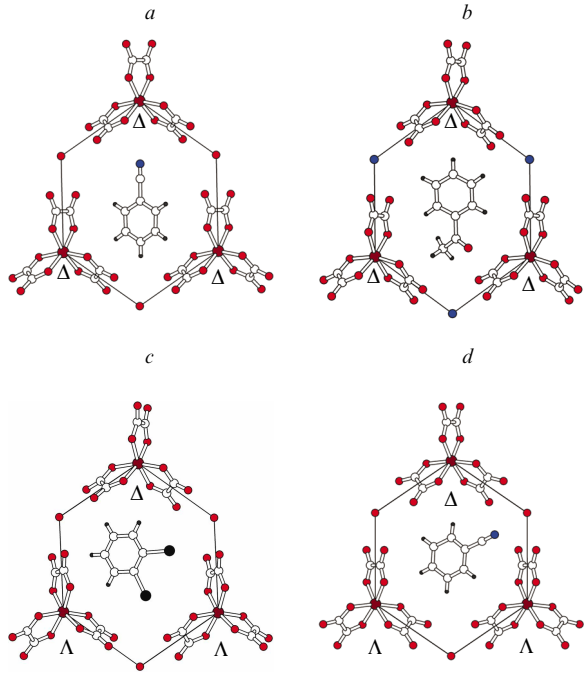


Figure 9. Alternation of optical isomers (Δ and Λ) of the chiral anion in the vertices of the hexagonal cells of the anionic layer for different phases of the (BEDT-TTF)$_4$A[Fe$(C_2O_4)_3$]·G family.[46] $A^+ = H_3O^+$ (*a*, *c*, *d*) and NH_4^+ (*b*); types of packing of radical cation layers: (*a*) β'', (*b*) $\alpha-\beta''$, (*c*) α–*pseudo*-κ, (*d*) *pseudo*-κ.

In the monoclinic and triclinic crystals with β''- and $\alpha-\beta''$-conducting layers, respectively, each anionic layer contains only one isomer of the chiral $[M^{3+}(C_2O_4)_3]^{3-}$ anion (Δ or Λ). Meanwhile, in orthorhombic crystals with a *pseudo*-κ type of packing and triclinic crystals with a α–*pseudo*-κ type of packing, each anionic layer contains both isomers (Fig. 9). The crystals as a whole are optically inactive. Day and co-workers[54,55] were able to obtain optically active BEDT-TTF crystals with tris(oxalato)metallate anions by using a reaction medium consisting of a guest solvent (G = $MeNO_2$ or CH_2Cl_2) mixed with a chiral solvent (R-carvone), which was not present in the structure. The stoichiometric composition of (BEDT-TTF)$_3$[NaCr$(C_2O_4)_3]\cdot$G salts thus obtained differed from that of (BEDT-TTF)A[M$(C_2O_4)_3]\cdot$G, but the structures of the anionic layers were similar. The enantiomers of the chiral $[Cr(C_2O_4)_3]^{3-}$ anion were distributed non-uniformly among the hexagon vertices of the honeycomb layer, namely, their ratios were 0.64 : 0.36 (G = $MeNO_2$) and 0.56 : 0.44 (G = CH_2Cl_2). The crystals showed a semiconducting temperature dependence.

V. Conducting properties of the monoclinic β''-(BEDT-TTF)$_4H_3O[M(C_2O_4)_3]\cdot$G crystals

The monoclinic (BEDT-TTF)$_4H_3O[M(C_2O_4)_3]\cdot$G crystals with the β'' type of packing of the radical cation layers were obtained with both magnetic and non-magnetic tris(oxalato)metallate anions (M^{3+} = Fe^{3+}, Cr^{3+}, Mn^{3+}, Ru^{3+}, Ga^{3+}) and with a large variety of guest solvents and mixtures G1–G2 of two guest solvents: G = PhX (X = Cl, F, Br, I, CN, NO_2), Py, HalPy (Hal = Cl, Br), 1,2-$Cl_2C_6H_4$, CH_2Cl_2, DMF; G1 = PhCN, G2 = PhX (X = Cl, F, Br, NO_2), 1,2-$Cl_2C_6H_4$ (see Tables 1–3). This is the largest group of isomorphous crystals both within the family in question and among all known molecular conductors based on radical cation salts formed of BEDT-TTF and its derivatives. The conducting properties of these crystals vary from semiconducting to metallic and to superconducting, depending on the chemical nature, size and shape of neutral solvent molecules.

V.1. Temperature dependence of the electrical resistance

The temperature dependence of the resistance for most monoclinic β''-(BEDT-TTF)$_4H_3O[M(C_2O_4)_3]\cdot$G crystals has a typical pattern. As the temperature decreases, the resistance decreases slightly before reaching a broad minimum at a temperature ranging from 40 to 150 K in various crystals and, after that, the resistance slowly increases until transition to the superconducting state[36–39,44,48,56,57] (Fig. 10 *a*,*c*) or to the lowest helium temperatures, as in the crystals with G = Py (M^{3+} = Fe^{3+}, Cr^{3+}) and PhCl.[38–42] In some crystals, the slow increase in the resistance starts immediately at room temperature (Fig. 10 *b*). The resistance decrease at $T < 2$ K in the crystals containing DMF as the solvent (M^{3+} = Fe^{3+}) is suppressed by a magnetic field (see the inset in Fig. 10 *c*), which is indicative of the superconducting transition.[58]

The β'' crystals containing tris(oxalato)chromate(III) and DMF as the guest solvent, unlike that for tris(oxalato)ferrate(III) salts, possess a metallic type of conduction over a broad temperature range (293–30 K). Upon further cooling, there is a moderate increase in the resistance (Fig. 11). This pattern of $R(T)$ dependence is rarely encoun-

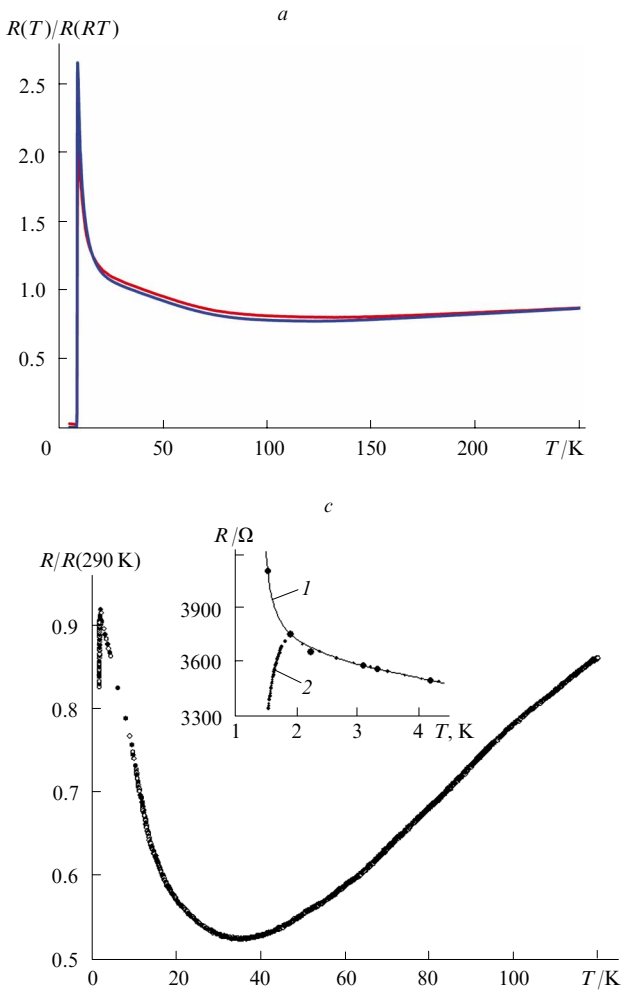


Figure 10. Temperature dependences of the resistivity of the crystals measured across the conducting layers.
(*a*) For two samples of β''-(BEDT-TTF)$_4$H$_3$O·[Fe(C$_2$O$_4$)$_3$]·PhCN crystals prepared by the procedure proposed in Ref. 44; $R(RT)$ is the resistance at room temperature;
(*b*) β''-(BEDT-TTF)$_4$H$_3$O[Ru(C$_2$O$_4$)$_3$]·PhBr, ρ is the resistivity;[48]
(*c*) β''-(BEDT-TTF)$_4$NH$_4$[Fe(C$_2$O$_4$)$_3$]·DMF;[58] the inset shows the behaviour of the resistance at $T < 4$ K in a 0.1 T magnetic field (*1*) and without a field (*2*).

tered in β'' salts of the given family. Despite the considerable decrease in the resistance on approaching helium temperatures (in some samples with $A^+ = NH_4^+$, the resistance decreases by a factor of 100 or more, see Fig. 11), these crystals do not undergo a transition to the superconducting state down to 0.5 K.[50, 59]

It is noteworthy that T_c of monoclinic crystals with $M^{3+} = Cr^{3+}$ is always 1.5 – 2 K lower than that of crystals containing the same guest solvent and $M^{3+} = Fe^{3+}$. Perhaps, the transition to the superconducting state in the crystals with $M^{3+} = Cr^{3+}$ obtained in DMF takes place at superlow temperatures. In the crystals with DMF and $M^{3+} = Fe^{3+}$, like in the crystals with $M^{3+} = Cr^{3+}$, the Shubnikov – de Haas magnetoresistance quantum oscillations were detected at low temperatures.[56, 58 – 60] This means that the ground state of crystals with $M^{3+} = Fe^{3+}$ is metallic, despite the increase in the resistance at temperatures below 25 – 40 K (see Fig. 10 *c*).

The temperature dependences of the resistance superconducting of crystals with two solvents, G1 – G2 (G1 = PhCN, G2 = PhF, PhCl, PhBr, $PhNO_2$, 1,2-$Cl_2C_6H_4$) are different. If G2 = PhBr (crystal **15**) or G2 = $PhNO_2$ (crystal **18**), $R(T)$ dependences are the same as for most superconducting crystals with one solvent: the resistance decreases to a certain minimum and then increases until the superconducting transition takes place (Fig. 12). The crystals with G2 = 1,2-$Cl_2C_6H_4$ (**16**) or

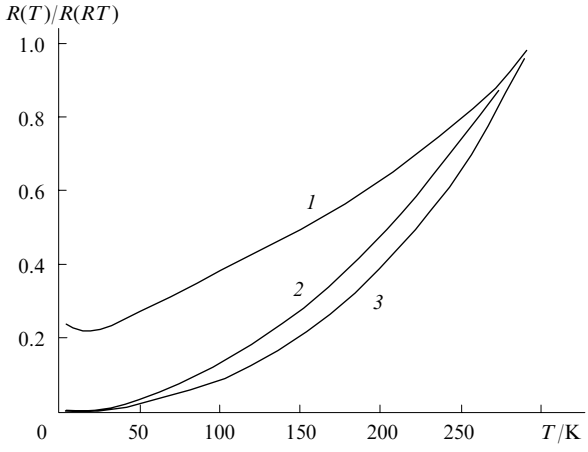


Figure 11. Temperature dependences of the resistance of the crystals of salt **34** (*1*) and two samples of salt **32** (*2*, *3*).[50]
The resistance was measured in the plane of conducting layers down to 4.2 K.

G2 = PhCl (**21**), show stable metallic or semimetallic behaviour until the superconducting transition occurs.

The low-temperature growth of the resistance observed in the β'' crystals is usually attributed to the electronic

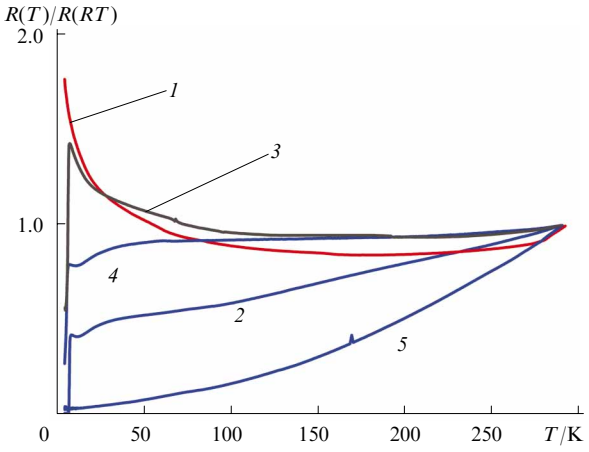


Figure 12. Temperature dependences of the relative resistance of β''-(BEDT-TTF)$_4$H$_3$O[Fe(C$_2$O$_4$)$_3$]·G crystals measured across the conducting layers down to 4.2 K.[44]
G: (*1*) (PhCN)$_{0.17}$(PhBr)$_{0.83}$ (**15**); (*2*) (PhCN)$_{0.86}$(1,2-Cl$_2$C$_6$H$_4$)$_{0.14}$ (**16**); (*3*) (PhCN)$_{0.8}$(PhNO$_2$)$_{0.2}$ (**18**); (*4*) (PhCN)$_{0.35}$(PhCl)$_{0.65}$ (**21**); (*5*) 1,2-Cl$_2$C$_6$H$_4$ (**22**).

inhomogeneity in the BEDT-TTF system, which is a consequence of partial charge ordering in these crystals with quarter-filled conduction band.[42, 57, 61, 62] In this case, the conductivity is defined by the relationship of conducting and localized electrons in the BEDT-TTF subsystem and the character of $R(T)$ dependence is determined by which component predominates.

According to a theoretical study,[63] the superconductivity in these crystals is mediated by charge ordering fluctuations. In this connection, it is worth noting that crystals **22** (see Fig. 12) and **32** (see Fig. 11), which show a stable metallic temperature dependence of resistance down to helium temperatures, do not undergo a transition to the superconducting state.

V.2. Effect of the size of neutral guest solvent molecules on the conducting properties

Study of the structures and properties of a lot of (BEDT-TTF)$_4$(H$_3$O$^+$)[M^{3+}(C$_2$O$_4$)$_3$]·G crystals provides the conclusion that there is a relationship between the size of the solvent molecules that are incorporated in the complex anionic layer and the electron transport. The superconducting crystals are formed with bulky solvent molecules, the superconducting transition temperature increasing with increasing size of these molecules.[30, 35 – 37] The dependence of the conducting properties on the size of the guest solvent molecule (G = PhCN, PhNO$_2$, PhBr, 1,2-Cl$_2$C$_6$H$_4$, Py, DMF) has been analyzed.[45] Structure analysis demonstrated that upon inclusion of relatively small guest molecules, some free space remains in the cavities of the anionic layer; this gives rise to positional disorder not only in the anionic layer, but also in the conducting radical cation layers of the crystals. As the temperature decreases, the positional disorder in the conducting layer of these crystals is retained[36, 43] or even increases;[41] this accounts for the absence of superconductivity in the crystals with relatively small guest solvent molecules.

Solvents with large molecular volume (PhCN, PhNO$_2$, PhBr, 1,2-Cl$_2$C$_6$H$_4$) occupy the whole cavity, their positions in the crystal being strictly defined. The thermal disorder of the terminal ethylene groups, which exists in these crystals at room temperature, completely disappears as soon as at 100 – 150 K. On lowering the temperature, the crystals containing PhCN, PhNO$_2$ or PhBr transition to the superconducting state; however, the superconducting transition temperature for the crystals with the same M^{3+} ion does not increase with increasing molecular volume of the solvent but, instead, decreases (Table 4); therefore, the effect of the size of the solvent molecule cannot be considered to be similar to the chemical compression effect.[42, 61] In the crystals with G = 1,2-Cl$_2$C$_6$H$_4$ (**22**), no superconducting transition was detected, although the dichlorobenzene molecule is larger than the molecules of solvents incorporated in superconducting crystals. Analysis of the structural data demonstrated that conducting properties of crystals of the given family are determined not so much by the volume of the guest solvent molecule as by the length of this molecule along the unit cell *b* axis.[45] This value increases in the series

$$\text{Py} < \text{DMF} < \text{1,2-Cl}_2\text{C}_6\text{H}_4 < \text{PhBr} < \text{PhNO}_2 < \text{PhCN}$$

which is in good agreement with the variation of the conducting properties of the crystals.

The data presented in Table 4 also imply that there is some volume of the solvent molecule that is optimal for superconductivity in the β'' crystals to arise. As the upper boundary of the volume required for superconductivity in these crystals, one can take the molecular volume of bromobenzene. The lower boundary corresponds to the volumes of DMF and Py, which, being present as the guest molecules, give rise to β'' crystals both exhibiting and not exhibiting the superconducting transition. For example, superconducting β''-(BEDT-TTF)$_4$H$_3$O$^+$[Fe(C$_2$O$_4$)$_3$]·DMF crystals are known ($T_c < 2$ K);[58] however, the replacement of Fe^{3+} by Cr^{3+} gives crystals [50] that do not exhibit superconducting transition (see Fig. 11). Among the crystals

Table 4. Conducting properties of the β''-(BEDT-TTF)$_4$A[Fe(C$_2$O$_4$)$_3$]·G crystals with guest solvent molecules of various sizes.[45]

G	A$^+$	V_G /Å^3	L_G /Å	Properties	Ref.
Py	Rb$^+$	115	2.43	Metal at $T > 1$ K	40
Py	H$_3$O	115	2.89	The same	41, 42
DMF	NH$_4$	115	3.39	Superconductor, $T_c < 2$ K	50, 58
1,2-Cl$_2$C$_6$H$_4$	H$_3$O	160	4.42	Metal at $T > 0.5$ K	45
PhBr	H$_3$O	155	4.61	Superconductor, $T_c = 4.0$ K	37
PhNO$_2$	H$_3$O	150	4.75	Superconductor, $T_c = 6.2$ K	35
PhCN	H$_3$O	145	5.32	Superconductor, $T_c = 8.5$ K	30

Note. The following designations are used: V_G is the volume of the solvent molecule calculated from the CCDC (The Cambridge Crystallographic Data Centre) data;[64] L_G is the length of the solvent molecule along the *b* axis in the anionic layer.

containing Py, the molecular volume of which is equal to that of DMF, both superconducting crystals ($M^{3+} = Ga^{3+}$)[36] and crystals without a superconducting transition ($M^{3+} = Fe^{3+}$, Cr^{3+})[40–42] were also found (see Table 1).

The effect of disorder in the anionic layer on the conducting properties can be followed in relation to crystals containing molecules of two guest solvents — PhCN and Py — in various ratios, $(PhCN)_x(Py)_{1-x}$.[65] The crystals containing PhCN have the highest superconducting transition temperature in the family; the BEDT-TTF ethylene groups in these crystals are ordered even at room temperature, whereas in the pyridine-containing crystals, complete ordering of ethylene groups is not observed down to $T = 30$ K (Ref. 36), and these crystals ($M^{3+} = Fe^{3+}$) do not undergo superconducting transition down to 0.5 K.[42] If some of the benzonitrile molecules in the crystals are replaced by smaller pyridine molecules, the structural disorder both in anionic and in radical cation layers increases; at low degrees of replacement, this leads to decreasing T_c, and when 65% of the PhCN molecules have been replaced by pyridine, the superconducting transition in these crystals is fully suppressed.

In the salts containing PhCN mixtures with other solvents, the superconducting transition temperature is also determined by the degree of replacement of benzonitrile (G1) by another guest molecule (G2). When PhCN is replaced by 1,2-$Cl_2C_6H_4$ (14%) or $PhNO_2$ (20%) (see crystals **16** and **18** and Fig. 12), the T_c value varies slightly (7.2 and 6.6 K, respectively) as compared with T_c for the crystals containing only PhCN. The replacement of PhCN by PhF (60%) or PhCl (65%) (see crystals **20** and **21** and Fig. 12) leads to a further (although moderate) decrease in T_c (to 6 K), whereas in crystals **15** in which 83% of PhCN has been replaced by PhBr, the superconducting transition occurs below 4.2 K, like for the crystals containing only PhBr (see Table 1).[37]

VI. Conducting properties of triclinic $\alpha-\beta''$ and $\alpha-$*pseudo*-κ crystals

It has been mentioned above that triclinic crystals of the (BEDT-TTF)$_4A^+[M^{3+}(C_2O_4)_3]\cdot G$ family comprise two groups of bi-layered crystals, those with $\alpha-\beta''$ and with $\alpha-$*pseudo*-κ types of packing of the radical cation layers. Since the crystal structure of the first group of salts contains α- and β''-packed BEDT-TTF layers with a metallic type of conductivity, these salts could be expected to behave as organic metals. However, the $\alpha-\beta''$ crystals (except those of one salt, which was shown to undergo a metal/semiconductor transition) are semiconductors. The cause for this behaviour is unclear and this issue requires further research.

As regards the $\alpha-$*pseudo*-κ crystals, the temperature dependences of conductivity of these crystals measured along and across the conducting layers are of metallic type (Fig. 13).[44, 46, 47] Whereas such a behaviour of conductivity along the layers could have been suggested, the metallic type of behaviour in the transverse direction was unexpected, because the metallic α layers in these crystals are separated by a semiconducting *pseudo*-κ layer and two dielectric anionic layers. The study of the transport properties of $\alpha-$*pseudo*-κ crystals is of considerable interest for the understanding of the interlayer transport mechanism in layered molecular conductors.

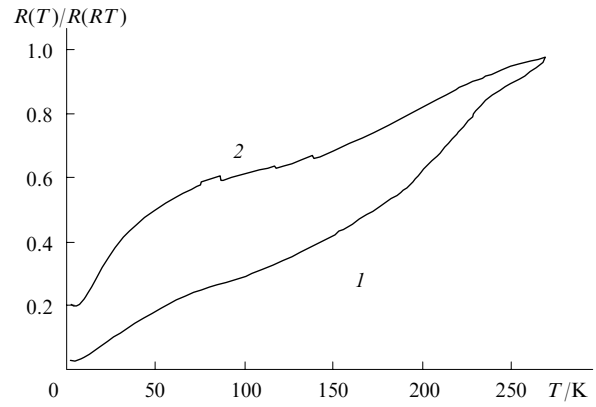


Figure 13. Temperature dependences of the resistance of bi-layered crystals **23** (*1*)[46] and **24** (*2*)[47] measured across the conducting layers.

VII. Conductivity and structural phase transitions in the crystals with halogen-containing guest molecules and β'' type of packing of radical cation layers

Apart from the superconducting phase transitions, which were discovered in many monoclinic crystals of the (BEDT-TTF)$_4A^+[M^{3+}(C_2O_4)_3]\cdot G$ family, crystals comprising monohalogen-substituted benzenes and pyridines undergo structural phase transitions at 180 – 250 K accompanied by symmetry lowering from monoclinic ($C2/c$) to triclinic ($P\bar{1}$). It is known that structural phase transitions in low-dimensional molecular conductors based on TTF derivatives can be accompanied by conformational ordering of the molecules, polymorphic transformations with a change in the conducting layer packing, partial positional rearrangement of the donor and anionic layers, transitions to charge-ordered states and so on. In the radical cation salts β''-(BEDT-TTF)$_4(H_3O^+)[Fe^{3+}(C_2O_4)_3]\cdot G$, a structural phase transition was first detected in a PhBr-containing salt;[37] however, neither unit cell parameters nor the crystal structure of the low-temperature phase were determined. Later, phase transitions were detected in many crystals containing monohalobenzenes or their mixtures with PhCN [G = PhF, PhCl, PhBr, $(PhCN)_{0.40}(PhF)_{0.60}$, $(PhCN)_{0.35}(PhCl)_{0.65}$ and $(PhCN)_{0.17}(PhBr)_{0.83}$],[39, 66] as well as in the monohalopyridine-containing crystals.[49]

X-Ray diffraction analysis of crystals β''-(BEDT-TTF)$_4H_3O[Fe(C_2O_4)_3]\cdot(PhCN)_{0.35}(PhCl)_{0.65}$ at room temperatures and at low temperature showed that the phase transition in this compound occurs at ~ 200 K. This transition affects little the crystal and electronic structures of the conducting layers and does not affect the positional ordering of the terminal ethylene groups of BEDT-TTF.[66] According to additional X-ray diffraction measurements at 190 and 100 K, no further ordering of ethylene groups in BEDT-TTF molecules takes place in the triclinic structure at 190 K (*i.e.*, immediately after the phase transition) compared to the monoclinic structure, whereas at 100 K, all ethylene groups are fully ordered.

The conducting properties of crystals do not change substantially in the phase transition region (Fig. 14). The sample demonstrates metallic behaviour over the whole

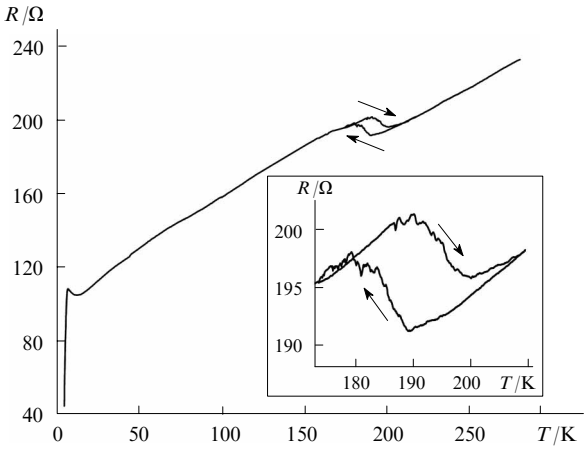


Figure 14. Interlayer resistance of superconducting β''-(BEDT-TTF)$_4$H$_3$O[Fe(C$_2$O$_4$)$_3$](PhCN)$_{0.35}$(PhCl)$_{0.65}$ crystals *vs.* temperature.[66]
The inset shows the hysteresis around the structural phase transition temperature.

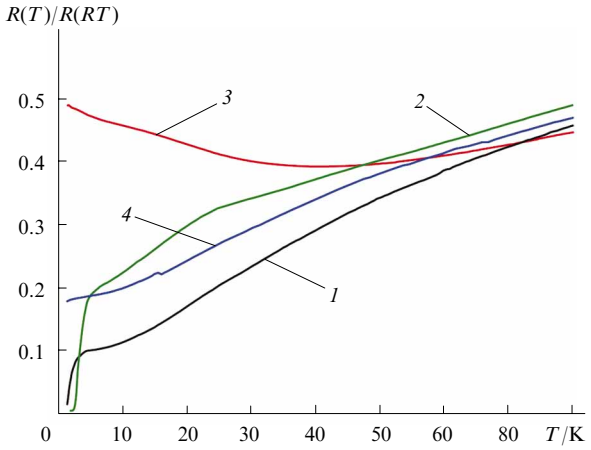


Figure 15. Temperature dependences of the relative resistance of β''crystals with monohalopyridines guest molecules.[49]
G: (*1*) 2-ClPy (**27**), (*2*) 2-BrPy (**28**), (*3*) 3-ClPy (**29**), (*4*) 3-BrPy (**30**).

temperature range before superconducting transition near 6 K. The $R(T)$ dependence showed a small jump of the resistivity with a hysteresis at about 200 K, *i.e.* around the temperature of the phase transition.

The main structural changes in these crystals on going from monoclinic to triclinic system consist in positional changes of anionic layer components. The greatest displacements relative to the positions in the monoclinic structure occur for molecule G. This provides the conclusion that halo-containing neutral guest molecules play the crucial role in the structural phase transition.

This conclusion was supported by the results obtained in the studies of the structural and transport properties of the crystals containing 2- and 3-halopyridines HalPy (Hal = Cl, Br) as solvents.[49] The use of these molecules provided not only new results about the phase transitions in the β''crystals but also data about the effect of the halogen position in the pyridine molecule on the structure and transport properties. The crystals of salts containing chlorine and bromine atoms in position 2 of the pyridine ring undergo phase transitions with decreasing symmetry from monoclinic to triclinic at 190 and 215 K, respectively, and the transition to the superconducting state with T_c = 2.4 – 4.0 and 4.3 K. Meanwhile, crystals in which the halogen atoms are in position 3 retain the monoclinic symmetry over the whole temperature range of the X-ray diffraction experiment (90 – 300 K) and do not switch to the superconducting state at $T >$ 0.5 K (Table 5, Fig. 15).

Table 5. Structural and conducting properties of the crystals of radical cation salts β''-(BEDT-TTF)$_4$(H$_3$O)[Fe(C$_2$O$_4$)$_3$]· HalPy.[49]

Salt	G	Structural properties	Conducting properties
27	2-ClPy	Transition from monoclinic ($C2/c$) to triclinic ($P\bar{1}$) symmetry at 215 K	Superconductor, T_c = 2.4 – 4.0 K
28	2-BrPy	Transition from monoclinic ($C2/c$) to triclinic ($P\bar{1}$) symmetry at 190 K	Superconductor, T_c = 4.3 K
29	3-ClPy	No structural transition	Metal at $T >$ 0.5 K
30	3-BrPy	The same	The same

According to X-ray diffraction data, the position of the halogen atom in the pyridine ring relative to nitrogen markedly affects the positioning of these isomers in the hexagonal cavities of the anionic layer. Figure 16 shows the positioning of 2-bromo- and 3-bromopyridine molecules disordered over two sites in the hexagonal cavities of crystals **28** and **30**. The 2-bromopyridine molecules in the crystals of salt **28** and 3-bromopyridine molecules in the crystals of salt **30** are shifted along a twofold axis (along *b*) in the opposite directions (this is shown by large arrows in Fig. 16). Therefore, the Br – Fe distance is shorter by 0.25 Å in crystal **28** [4.562(1) Å] than in crystal **30** [4.801(1) Å].

At room temperature, the structures of the radical cation layers of all four salts (**27** – **30**) are typical of monoclinic crystals of this family: β'' type packing with two crystallographically independent BEDT-TTF molecules (*A* and *B* in Fig. 17 *a*). The charge state of each of them is +0.5, which follows from the composition of the salts and bond length distribution in the TTF core [the lengths of the central C=C bonds in molecules *A* and *B* are 1.366(3), 1.365(3) Å in **28** and 1.364(3), 1.370(3) Å in **30**]. Both terminal ethylene groups in radical cation *B* are disordered over two sites (with occupancies of 0.70/0.30 in **28** and 0.65/0.35, 0.67/0.33 in **30**), whereas *A* radical cation is fully ordered at room temperature.

On cooling, a phase transition takes place in crystal **28** at 190 K. The new triclinic structure comprises four independent π-donor molecules, which form two non-equivalent conducting layers (Fig. 18): *T*1 layer is composed of *A*1 and *B*1 radical cations and *T*2 layer consists of *A*2 and *B*2 radical cations. The phase transition is accompanied by partial ordering in the *B*1 and *B*2 π-donors, which are disordered at room temperature. One of the terminal ethylene groups of each π-donor becomes completely ordered, whereas the other ethylene group remains disordered over two sites with occupancies of 0.52/0.48 and 0.67/0.33 for *B*1 and *B*2, respectively. However, there is no significant differ-

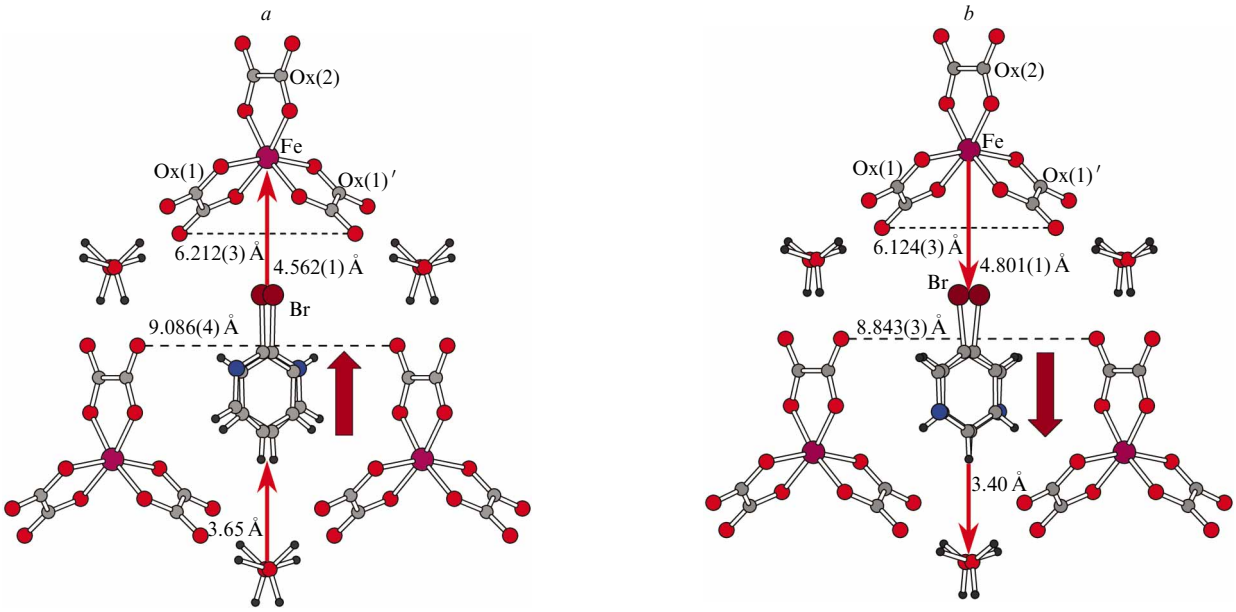


Figure 16. Hexagonal cell of the anionic layer in crystals **28** (*a*) and **30** (*b*).[49]

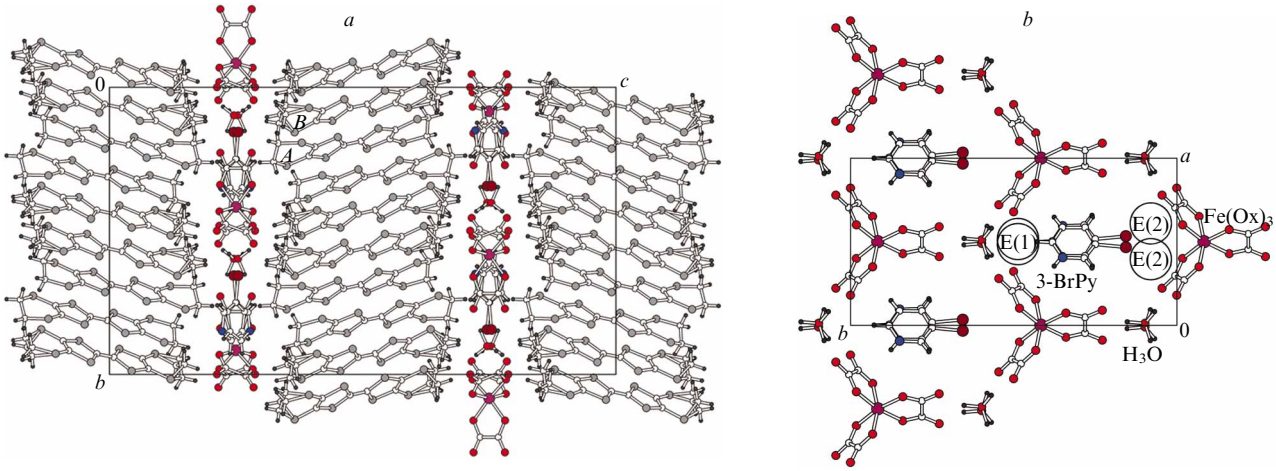


Figure 17. Monoclinic structure of crystal **28** at room temperature.[49]
(*a*) projection of the structure along the *a* axis; (*b*) projection of the anionic layer along the *c* axis [positions of the disordered terminal ethylene groups E(1) and E(2) of *B* π-donor located above and below the anionic layer plane are shown].

ence between the BEDT-TTF charge in the *T*1 and *T*2 layers.

Unlike crystals **28** with 2-bromopyridine, in crystals **30** with 3-bromopyridine, the structural phase transition does not take place down to 100 K and disorder is retained in both terminal ethylene groups of the *B* radical cation. The salts with 2-chloropyridine (**27**) and 3-chloropyridine (**29**) exhibit the same features as salts **28** and **30** with bromopyridines. The phase transition in the crystal **27** occurs at 215 K, whereas in the crystal **29**, this transition does not occur down to 90 K.

The calculations of electronic structures of monoclinic and triclinic phases demonstrated that the band structures of these phases are similar. The minor differences between these structures cannot be responsible for the absence of superconductivity in crystals **29** and **30**. Apparently, the loss of superconductivity is caused by the existence of a more pronounced structural disorder in these crystals at low temperature compared with crystals **27** and **28**. The superconductivity of low-dimensional conductors is known to be highly sensitive to the disorder. The terminal ethylene groups of one of the independent BEDT-TTF radical cations (*B*) are disordered at room temperature in all four salts and are located above and below the free space of the hexagonal cavity, near the disordered solvent molecules (Fig. 17 *b*). The ordered groups of the other BEDT-TTF molecule (*A*) are located more closely to the ordered anions. In the triclinic superconducting salts **27** and **28**, disordered π-donors (*B*) become partly ordered; complete ordering is observed at 120 K in the E(1) group of the *B*1 molecule and in the E(2) group of the *B*2 molecule (Figs 17 *b* and 18). In non-superconducting salts **29** and **30**, the *B* π-donor remains disordered at low temperatures. It is also noteworthy that increase in the distance between the halogen atom and the

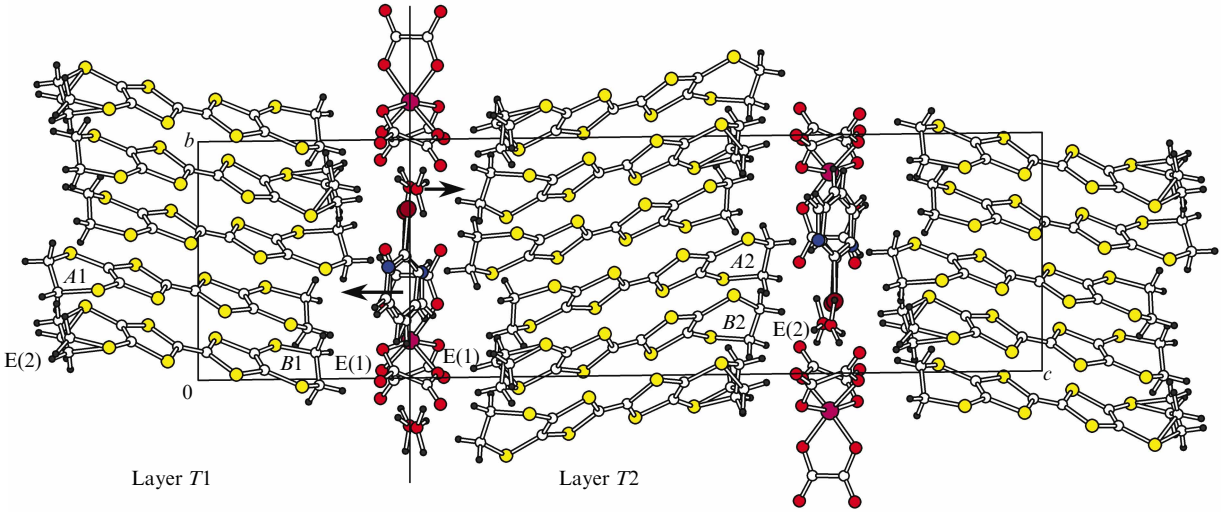


Figure 18. Projection of the triclinic structure of salt **28** along the *a* axis at 120 K.[49]
The shift of the 2-bromopyridine molecule and H_3O^+ from the anionic layer plane is shown by the arrows. The terminal ethylene groups E(1) and E(2) of the disordered π-donors *B*1 and *B*2 are designated as in Fig. 17 *b*.

iron atom by 0.25 Å in structures **29** and **30** compared with structures **27** and **28** gives rise to a greater free space near the halogen atoms in the hexagonal cavities of **29** and **30** and, hence, brings about additional disorder in these crystals.

Thus, different positions of different isomers of monohalopyridines in the hexagonal cavity have an influence on the degree of ordering of the BEDT-TTF ethylene groups in the conducting layers and, as a consequence, on the superconducting transition.

VIII. Conclusion

The interest in the family of four-component radical cation salts, $(BEDT\text{-}TTF)_4A^+[M^{3+}(C_2O_4)_3]\cdot G$, is still fairly high, which is due both to the possibility of modifying their structures and magnetic and conducting properties by varying the components A, M and G and to the particular aspects of their properties. The performed analysis demonstrated that the size, shape and chemical nature of the guest solvent molecule are the key factors determining the symmetry of crystals and the type of packing of the BEDT-TTF conducting layers. The variation of these solvent molecules gave rise to the bi-layered BEDT-TTF salts composed of alternating BEDT-TTF layers with different (α and β'' or α and *pseudo*-κ) types of packing and supramolecular $\{A^+[M^{3+}(C_2O_4)_3]\cdot G\}^{2-}$ anionic layers sandwiched between them. Studies of the crystal and electronic structures of the $\alpha-\beta''$ salts indicate that both conducting layers should exhibit metallic properties, whereas the *pseudo*-κ layer in the α–*pseudo*-κ salts is dielectric. However, measurements of the temperature dependences of the resistance $R(T)$ demonstrated that four out of five $\alpha-\beta''$ salts are semiconductors, while the fifth one undergoes the metal/semiconductor transition at 150 – 170 K. Conversely, α–*pseudo*-κ salts are stable metals down to helium temperatures. Currently, many radical cation salts based on BEDT-TTF and its derivatives are known; however, there are few bi-layered salts among them.[46, 47, 52, 53, 67 – 70] The bi-layered salts provoke a lot of interest regarding both the study of the interlayer transport mechanism[68] and the increase in T_c associated with the possible interplay of various conducting layers within the same crystal lattice. An example of such interplay is the $\alpha'-\kappa$-$(BEDT\text{-}TTF)_2Ag(CF_3)_4\cdot C_2H_3Cl_3$ radical cation salt in which metallic κ layers alternate with dielectric α′ layers.[69] There are two superconducting polymorphs of this salt, those with $\kappa-\alpha'_1$- and $\kappa-\alpha'_2$-packed conducting layers and with T_c values of 9.5 and 11 K, respectively, which is much higher than T_c of the third polymorph incorporating conducting layers with only *k* type of packing (T_c = 2.6 K).[69, 70]

Further studies of the conducting properties of the $(BEDT\text{-}TTF)_4A^+[M^{3+}(C_2O_4)_3]\cdot G$ salts should address a number of problems, the following being most important:

— dynamic charge localization in monoclinic β'' crystals and its relationship with superconductivity;

— contradiction between the type of packing of BEDT-TTF layers in the triclinic $\alpha-\beta''$ crystals and the conducting properties of the crystals;

— metallic conductivity of α–*pseudo*-κ crystals along the *c* axis where the 'metallic' α layers are separated by three dielectric layers (one *pseudo*-κ layer and two anionic layers);

— effect of paramagnetic ions in the anionic subsystem on the character of electronic states in the conducting radical cation system.

Comparison of the superconducting transition temperatures in the series of monoclinic β'' crystals containing supramolecular $\{H_3O[M(C_2O_4)_3]PhNO_2\}^{2-}$ anions and paramagnetic Cr^{3+} and Fe^{3+} ions and the diamagnetic Ga^{3+} ion showed increasing T_c: 5.8, 6.2 and 7.5 K, respectively (see Table 1). In another series of salts with $M^{3+} = Fe^{3+}$, Cr^{3+}, Ga^{3+} and G = Py, superconducting transition was found only in the crystals with diamagnetic Ga^{3+} ion (see Table 1). A change in T_c in one case and suppression of the superconducting transition in the other case may be attributable to the magnetic nature of the Cr^{3+} and Fe^{3+} ions. However, this issue requires targeted investigation.

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