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Organic Metals and Superconductors Based on Tetrathiofulvalene Derivatives

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The latest advances in the synthesis and research into organic metals based on various heterocyclic systems are examined. The influence of the structure of the organic donor and of the size and geometry of the anions on the electrophysical properties of compounds of this series and the conditions governing the appearance of their superconductivity are discussed in relation to compounds of the class of tetrathiofulvalenes.
The bibliography includes 150 references.

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I. INTRODUCTION

A new branch of synthetic organic chemistry and the chemistry of coordination compounds (associated with solid state physics), whose task is to synthesise and investigate new materials, which have been called organic metals, has developed vigorously during the last decade. Synthetic organic metals are highly anisotropic and in a certain temperature range behave like "true" metals; on the other hand, they have many unusual electrical, magnetic, and electronic properties[1-4].

The range of compounds on the basis of which synthetic metals can be obtained is fairly wide; further new substances, which are the principal components of organic metals, are being continually synthesised.

Many new studies (their number is increasing rapidly) of square planar transition metal complexes, which also exhibit the properties of one-dimensional synthetic metals under certain conditions have been published[5-8]. The dithiolate complexes of transition metals[9,10] and phthalocyanine[12,14] and porphyrin[11,13] derivatives are being widely investigated. Research into polymeric and electrically conducting materials is developing particularly vigorously. A realistic hope for the creation of fundamentally new technological materials has been a stimulating factor in this field[15-17]. A series of purely inorganic compounds also exhibit metallic conductivity [18,19].

The largest and vigorously developing class of compounds consists of organic metals based on radical-ion salts (RIS) and charge-transfer complexes (CTC) of various electron-donating and electron-accepting compounds. Among numerous thoroughly investigated radical-anion salts based on tetracyanoquinodimethane (TCQM) [20] and other electron acceptors[21], the organic metals which conduct electric current most effectively contain quinolinium, acridinium, and phenazinium cations and are radical-ion salts with a partially reduced TCQM molecule. The conduction in these salts takes place via a stack of TCQM radical-anion species.

Organic metals consisting of compounds with two conducting stacks (electron-donating and electron-accepting) have been thoroughly investigated. In this group of charge-transfer complexes, the salt TTF.TCQM (where TTF = tetrathiofulvalene) and all possible TTF derivatives capable of forming radical-ion salts with TCQM (and other organic acceptors) have been most thoroughly investigated[2,3,23]. CTC or RIS with TCQM have been obtained for the majority of electron-donating compounds listed in Table 1. Many important features characteristic of organic metals have been established precisely on the basis of the study of the radical-ion salts of certain TTF derivatives and other electron donors with TCQM. This has been reflected in a series of review publications[3,4,22,24,25] covering extensive factual data.

The latest advances in the field of organic metals are associated with the study of the radical-cation salts based on tetrathiofulvalenes, tetrathiotetracenes, and other heteroaromatic compounds in which conduction takes place solely via a stack of organic electron-donating molecules. These compounds proved to be the most convenient models for the investigation of the nature of organic metals and their transport properties[3,4,30].

Numerous radical-ion salts of TTT,[26] have been obtained in the series of tetrathiotetracenes TST,[27,28] and TTeT.[29]† The salts $(TST)_2Cl(Br)$ have record conductivities at room temperature ($\sigma = 2\times10^3\ \Omega^{-1}\ cm^{-1}$) and their metallic state is stable down to 1.5 K.[27] These results have been described in a number of reviews[3,30,31].

This review deals with organic metals comprising only tetrathiofulvalenes with inorganic anions. The first organic superconductors based on sulphur- and selenium-containing TTF derivatives have in fact been obtained among compounds of this series[32,33].

II. ORGANIC METALS BASED ON ELECTRON-DONATING COMPOUNDS. CONDITIONS GOVERNING THE EXISTENCE OF ORGANIC METALS

The principal trend in the development of the synthetic chemistry of organic metals is associated with the formation of new heteroaromatic compounds[34,35], with the introduction of various substituents into electron-donating and electron-accepting compounds and the study of the influence of these substituents on the conducting properties[36], and with the replacement of sulphur by selenium[37] and tellurium[38] in compounds of a single series. The endeavour to obtain a series of sulphur-, selenium-, and tellurium-containing compounds

† The abbreviations are defined in Table 1 (Ed. of Translation).

is due to the characteristic features of the structure of organic metals: the possibility of the movement of an electron through a stack of organic molecules is due to the overlap of the wave functions of the unpaired electrons of the heteroatoms and such overlap increases with increase in the size of the heteroatoms in the organic compound.

Table 1. Electron-donating compounds from which organic metals have been obtained.

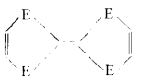
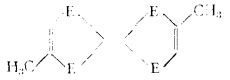
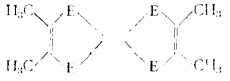
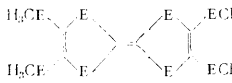
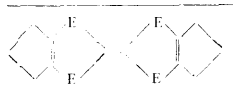
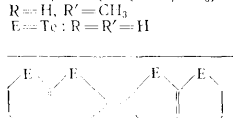
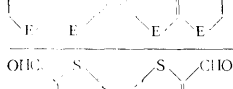
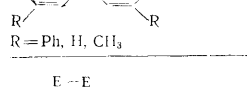
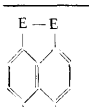
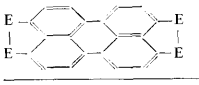
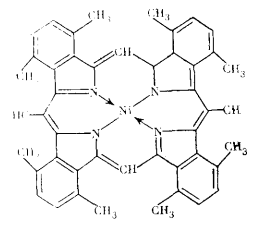
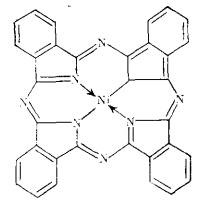
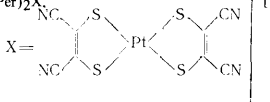
Formula	Name of compound	Refs.
	E = S, tetrathiofulvalene (TTF) E = Se, tetraselenofulvalene (TSF)	[42] [42]
	E = S, dimethyltetrathiofulvalene (DMTTF) E = Se, dimethyltetraselenofulvalene (DMTSF)	[42] [42]
	E = S, tetramethyltetrathiofulvalene (TMTTF) E = Se, tetramethyltetraselenofulvalene (TMTSF)	[42] [42, 43, 44, 150]
	E = S, tetrathiomethoxytetrathiofulvalene (TTMTTF) E = Se, tetraselenomethoxytetraselenofulvalene (TSMTSF)	[42] [42]
	E = S, hexamethylenetetrathiofulvalene (HMTTF) E = Se, hexamethylenetetraselenofulvalene (HMTSF) E = Te, hexamethylenetetratelluro-fulvalene (HMTTeF)	[42] [42] [45]
	E = S, dibenzotetrathiofulvalene (DBTTF)	[42]
E = S, Se: R = R′ = H, CH_3; R = H, R′ = CH_3 E = Te: R = R′ = H	E = Se, dibenzotetraselenofulvalene (DBTSF) E = Te, dibenzotetratellurofulvalene (DBTTeF)	[37, 46] [38]
	E = S, bis(ethylenedithiolo)tetrathio-fulvalene (BEDT-TTF) E = Se, bis(ethylenediselenoslo)tetra-selenofulvalene (BEDS-TSF)	[47] [48]
	Tetraformyltetrathiofulvalene (TFTTF)	[49]
 R = OCH_3, H	E = S, dinaphthotetrathiofulvalene (DNTTF) E = Se, dinaphthotetraselenofulvalene (DNTSF)	[50] [50]
 R = Ph, H, CH_3	E = O, bipyranylidene (BP) E = S, bithiopyranylidene (BTP) E = Se, biselenopyranylidene (BSP) E = Te, bitelluropyranylidene (BTP)	[51] [51, 52] [53] [54]
	E = S, tetrathiotetracene (TTT) E = Se, tetraselenotetracene (TST) E = Te, tetratellurotetracene (TTTeT)	[55] [56] [29, 57]
	E = S, tetrathioanthracene (TTA) E = Se, tetraselenoanthracene (TSA)	[58] [58]

Table 1 (cont.)

Formula	Name of compound	Refs.
	E = S, tetrathionaphthalene (TTN)	[59]
	E = S, tetrathioperylene (TTP) E = Se, tetraselenoperylene (TSP)	[60, 61] [62]
	Octamethylenetetrabenzo-porphyrins (OMTBP)	[11, 13]
	Phthalocyanines (PC)	[12, 14]
Naphthalene (Naphth)	$(Naphth)_2PF_6$	[63]
Naphthalene Pyrene Fluoranthene	$(Arene)_2X$, X = PF_6^-, AsF_6^-, SbF_6^-, or BF_4^-	[15, 64]
Perylene (Per)	$(Per)_2(PF_6)_{1.1}.0.8CH_2Cl_2$ $(Per)_2(AsF_6)_{1.1}.0.7CH_2Cl_2$ $(Per)_2(PF_6)_{1.4}.0.6THF$ $(Per)_2(AsF_6)_{1.5}0.5THF$ $(Per)_2X$, X = 	[65] [65] [65] [65] [66]

Both electron-donating and electron-accepting compounds which are components of organic metals have a number of characteristic features[3,39,40], which have been established as a result of the investigation of extensive experimental data; the conditions governing the existence of the stabilised metallic state are constantly being extended and refined.

Table 1 presents the principal classes of heterocyclic electron-donating compounds from which organic metals have been obtained at the present time and are being investigated. The molecular and crystal structures of the components of organic metals must satisfy the following requirements.

(1) Their molecule must be planar in the neutral and ionic states; there is a possibility of a slight deviation (2-4°) from planarity of the ring, which creates conditions for the closest packing of the molecules in the crystal. The intermolecular interaction of the components in the conducting organic stack takes place via the overlap of the molecular π orbitals and is described by the overall wave functions of the unpaired electrons delocalised along the entire molecule.

(2) Their molecules must be symmetrical in order to eliminate the possibility of the appearance of a high random potential which might cause a transition of the system to the dielectric state. A weak electronic or structural disorder may stabilise the metallic state.

(3) The compounds considered must be packed in regular stacks. The movement of electrons takes place along the stack of organic molecules more readily than in the other two directions (the substances are anisotropic in the crystal state).

(4) The distances between the molecules in the stack must be identical and minimal to ensure the non-activated movement of electrons along the stacks.

(5) Apart from the shortened distances between the molecules within the stack, shortened distances between individual stacks are necessary for the stabilisation of the metallic state down to low temperatures and for the occurrence of the superconducting transition.

The electronic structures of the compounds must also have a series of characteristic features.

(1) The presence of unpaired electrons in the system is essential.

(2) Partial charge transfer must take place. Moderately strong electron donors and acceptors satisfy this criterion. The difference between the oxidation-reduction potentials of the electron donor and acceptor must be minimal[39,41].

(3) A minimal Coulombic repulsion energy is necessary to destabilise the transition to the Mott insulator state[39,41].

III. ORGANIC METALS AND SUPERCONDUCTORS BASED ON TETRATHIOFULVALENE DERIVATIVES

1. Organic Metals Based on Unsubstituted Tetrathiofulvalene and Tetraselenofulvalene With Inorganic Anions

The synthesis in 1970 [67] of tetrathiofulvalene, a heterocyclic compound, initiated the study of the enormous class of compounds based on it[2,3]. The crystals of neutral TTF are made up[68] of stacks of its molecules packed in such a way that the character of the structure predetermines the possibility of the insertion of small anions in the channels between the TTF stacks.

Interesting studies have been made on the radical-ion salts of unsubstituted TTF with the halogens. TTF derivatives with the singly charged Cl^-, Br^-, and I^- anions can be obtained by the direct oxidation of standardised TTF solutions in acetonitrile or CCl_4 with standard solutions of Cl_2, Br_2, and I_2 in the same solvents[69,70]. The photochemical reaction

$$TTF + CCl_4 \xrightarrow{h\nu} (TTF)Cl_n$$

can yield TTF chlorides[71]. TTF halides can also be obtained in the electrochemical generation of the TTF^+ radical-cation with subsequent addition of an alkylammonium salt containing Cl^-, Br^-, or I^-.[69] Under certain conditions, there is a possibility of the reverse reduction of the TTF^+ radical-cation with formation of the Br_3^- anion and the initial TTF [72]:

$$TTF^+ + Br^- \rightarrow TTF^0 + Br_3^-.$$

A characteristic feature of the reaction of TTF with the halogen is the formation of the compound $(TTF)X_n$, where $X = Cl^-$, Br^-, or I^- with different values of n. For $n = 1$, one electron is removed from each TTF molecule and the radical cation salt $(TTF^+)X^-$ with complete charge transfer is formed. When $n = 2$, dicationic salts are obtained, two electrons are removed from each TTF molecule on oxidation, and the salt $(TTF)^{2+}X_2$ is produced[69]. However, the number of electrons transferred from an electron-donating TTF molecule to the acceptor is frequently non-integral and is actually less than unity. For $n < 1$, compounds with different stoichiometric compositions are obtained and n can vary continuously within a certain range, while the physical properties of the compound do not change significantly.

The compounds $(TTF)X_n$ where X = halogen and $n < 1$, have been isolated and characterised in detail[69] and the parameters of their unit cell have been published. The phase with n in the range $0.7 < n < 0.8$, obtained for all three halogens indicated, is the most stable[69]. The structure of compounds having this composition [and in general of all the non-stoichiometric compounds $(TTF)X_n$] is characterised by the presence of two independent sublattices: the cationic sublattice consisting of TTF molecules packed regularly in stacks and the anionic sublattice consisting of inorganic anions. The channels between the TTF stacks are filled with the Cl^-, Br^-, or I^- anions distributed with different densities, which determine the non-stoichiometric composition of the compounds $(TTF)X_n$. Fig. 1 presents the structure of the compound $(TTF)Br_{0.76}$;[70] $n = 0.76$ corresponds to the maximum Br^- content on $(TTF)Br_{0.71-0.76}$. The structure contains two separate sublattices; the first consists of stacks of TTF molecules arranged along the conducting axis and the anions Br^- are arranged in the channels between the TTF molecules (second sublattice). The unit cell parameters are constant in the range $n = 0.71-0.76$. The distances between the TTF stacks are regular and equal to 3.57 Å.

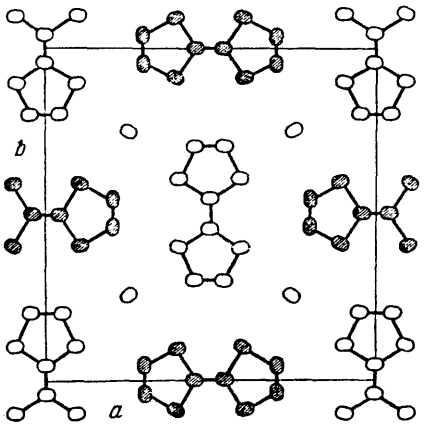


Figure 1. The structure of $(TTF)Br_{0.76}$.[70] Projection along the direction of the radical-cation TTF stacks.

The conductivities of the compounds $(TTF)X_n$ with halide ions are fairly high (Table 2). However, on decrease of temperature, all these compounds undergo the metal-, insulator transition at temperatures in the range 170–270 K and pass to the dielectric state. This is associated with a rearrangement of the structure of these compounds occurring as the temperature is reduced—the so-called Peierls transition takes place[78]. Despite the partial charge transfer, the conductivities of the compounds $(TTF)X_{0.67}$ with $X = ClO_4^-$ or BF_4^- are low, apparently because of the irregular packing of the electron-donating TTF molecules in the stack.

A series of non-stoichiometric TTF derivatives have been isolated electrochemically; one of them, namely $TTF(NO_3)_{0.55}$, has been characterised fairly completely and investigated[80].

Like the $(TTF)X_n$ with halide anions, this non-stoichiometric compound is made up of individual TTF stacks; the NO_3^- anions are distributed in the channels between the stacks of TTF molecules. While the compound has a fairly high conductivity at room temperature ($\sigma = 1200\ \Omega^{-1}\ cm^{-1}$), it undergoes a Peierls type metal → dielectric transition at 180 K.[80]

Apart from the non-stoichiometric compounds indicated in Table 2, radical-cation salts having the composition (TTF)X or $(TTF)_2X^{2-}$, where $X = Cl^-$, Br^-,[69] NO_3^-, BF_4^-, ClO_4^-,[82] $CuBr_3^-$, $AuCl_2^-$, $Cu(NO_2)_2^-$, $TiCl_4^{2-}$, $SnCl_6^{2-}$, or $RuCl_5^{2-}$,[84] the salts (TSF)X, where $X = Cl^-$[88] or I_3^-,[85] and the dicationic salts $(TTF)X_2$ or $(TTF)X^{2-}$, where $X = Cl^-$, Br^-,[69] NO_3^-, BF_4^-, ClO_4^-,[81,82] $CuCl_4^{2-}$, or $AuCl_4^{2-}$,[84] have been obtained.

The conductivities of the compounds (TTF)X with complete charge transfer are low and amount to 10^{-4}–$10^{-7}\ \Omega^{-1}\ cm^{-1}$. The compounds $(TTF)X_2$ are always insulators.

When TTF is oxidised by copper(II) chloride, several products are formed, depending on the solvent employed[81]; compounds with the copper-containing $CuCl_2^-$ anion are obtained (Table 2). Raman spectroscopic studies of these compounds have shown that the compounds $(TTF)_3(CuCl_2)_5$ contain both TTF^+ and TTF^{2+}; the latter is the only example of a compound with a mixed valence incorporating the TTF^{2+} dication. The compound $(TTF)(CuCl_2)$ contains only TTF^+, while $(TTF)(CuCl_4)^{2-}$ contains only the TTF^{2+} dication[81].

Table 2 Characteristics of the radical-ion salts based on unsubstituted tetrathiofulvalene and tetraselenofulvalene with inorganic anions.

Compound	σ, $\Omega^{-1}\ cm^{-1}$	T_t^*, K	Refs.
$(TTF)Cl_{0.77-0.91}$	4	271	[69, 71, 76]
$(TTF)Br_{0.71-0.76}$	300—550	180	[69, 73]
$(TTF)I_{0.69-0.72}$	100—450	200—270	[74]
$(TTF)(SCN)_{0.54}$	500—750	170	[75]
$(TTF)(SeCN)_{0.54}$	500—750	170	[75]
$(TTF)(NO_3)_{0.55}$	170; 1200	180	[80]
$(TTF)(BF_4)_{0.67}$	10^{-6}	—	[77, 82, 84]
$(TTF)(ClO_4)_{0.67}$	10^{-5}	—	[82]
$(TTF)_2(NO_3)$**	$5\cdot10^{-2}$	—	[81]
$(TTF)_3(CuCl_2)_5$	10^{-5}	—	[81]
$(TTF)CuCl_4$	10^{-5}	—	[81]
$(TTF)(CuBr_3)_{0.4}$	$4\cdot10^{-2}$	—	[84]
$(TTF)(CoCl_3)_{0.4}$	$4\cdot10^{-2}$	—	[84]
$(TTF)(PtCl_6)_{0.33}$	10^{-2}	—	[84]
$(TTF)_{0.6}[Ir(CO)_2Cl_2]$	10^{-2}	—	[79]
$(TSF)Br_{0.8}$	10	—	[88]
$(TSF)I_{0.8}$	300	—	[85]
$(TSF)(ClO_4)_{0.67}$	10^{-3}; 10^{-2}	—	[82, 110]
$(TSF)(BF_4)_{0.67}$	$5\cdot10^{-3}$	—	[82]
$(TSF)(NO_3)_{0.8\pm0.02}$	$5\cdot10^{-2}$	—	[82]

*T_t = metal–dielectric transition temperature.

**The composition of this compound apparently differs from $(TTF)_2(NO_3)$.

The oxidation of TTF in acetonitrile by the copper(II) salts CuX, where $X = ClO_4$, BF_4, or NO_3, leads to the formation of compounds having three different stoichiometric compositions depending on the reactant ratio: $(TTF)X_n$, (TTF)X, and $(TTF)X_2$[81,82] (Table 2).

Two types of packing of the TTF molecules have been observed[83] in the trichloromercurate radical-cation salts $(TTF)HgCl_3$, while the mercury-containing anions form either the dimers $(Hg_2Cl_6)^{2-}$ or polymer chains made up of $(HgCl_3)_n^{n-}$. The distance between the planes of the TTF molecules is 3.6 Å, which is analogous to the distances in $(TTF)Cl_{0.92}$[76] and $TTFBr_{0.76}$,[70] or 3.45 Å, as in the fully oxidised TTBr.[70] The structural analogies and X-ray diffraction data have led to the conclusion[83] that TTF is present in the $(TTF)HgCl_3$ salt in two different oxidation states. This has also been confirmed by Raman spectroscopy[83,84].

Very few compounds of the selenium analogue, namely the unsubstituted TSF, with inorganic anions have been investigated (Table 2), which is due to the difficulty of synthesising the initial TSF and the low conductivities of the compounds obtained. Thus, while the conductivity of the compound $(TSF)I_{0.8}$ at room temperature is comparatively high, if the temperature is reduced it behaves as a semiconductor[85] with an activation energy of conduction $E = 0.149$ eV.

In connection with the discovery of the superconductivity of the salts $(TMTSF)_2X$ ($X = BF_4$, ClO_4, NO_3 or PF_6),[105] the properties of the unsubstituted TSF combined with singly charged anions are of interest. The non-stoichiometric salts $(TSF)X_{0.67}$, where $X = ClO_4$ or BF_4, which are analogues of the salts of unsubstituted TTF,[77,84] have been obtained[82] by oxidising TSF with copper(II) salts. Salts having the 2:1 composition could not be isolated. X-Ray diffraction study of the salt $(TSF)(ClO_4)_{0.67}$[87] showed that the stack of the TSF molecules is divided into triads of molecules in terms of the type of overlap and that this apparently is the immediate cause of the significant decrease of the conductivity of this salt[86] (Table 2).

2. Organic Metals Based on Dibenzotetrathiofulvalene

The introduction of two benzene rings into the TTF molecule increases the extent of its π-electron system and the electron-donating capacity of dibenzotetrathiofulvalene (DBTT) then decreases compared with the unsubstituted TTF.[89] In the neutral state the DBTTF molecules are packed in regular stacks with interplanar distances between the molecules of 3.544 Å.[90]

The interaction of DBTTF with chlorine and bromine leads to the formation of mixtures of products with different stoichiometries[91,92], as for the unsubstituted TTF.[69] Individual single crystal compounds with chlorine were not isolated and compounds having the formula $(DBTTF)Cl_{0.7-1.0}$ were obtained. When DBTTF : Br = 1 : 1.2 in the reaction mixture, the compound $(DBTTF)Br_{1.2}$ is obtained; other compounds with bromine have the composition $(DBTTF)Br_{0.8-1.0}$.[91]

The reaction of DBTTF with iodine has been investigated in nitrobenzene and acetonitrile[91]. For the reactant ratio DBTTF : I = 1 : 0.5 in nitrobenzene, the compound $(DBTTF)_2I_3$ was isolated; further increase of the amount of iodine leads to the compound $(DBTTF)I_3$. In acetonitrile, the salt $(DBTTF)_2I_3$ was isolated for the ratio DBTTF : I = 1 : 2 and in the presence of a still greater excess of iodine (up to the ratio 1 : 10) the salt $(DBTTF)I_3$ was obtained. Compounds having the compositions $(DBTTF)I_{0.5}$ and $(DBTTF)I_{0.8}$ have been obtained in acetonitrile[94].

The compound $(DBTTF)I_3$ has been investigated by X-ray diffraction[93] (Fig. 2). Stacks made up of alternating groups of three DBTTF molecules and two linear I_3^- anions are characteristic of the structure. The linear I_3^- ions are accommodated in the channels between the mixed stacks. The S–S distance in the structure is shortened to 3.50 A; in addition, there are a series of shortened distances between S atoms and I_3^- groups. This structure of the compound $(DBTTF)I_3$ differs from that of the compounds of the unsubstituted TTF with the halogens, in the structure of which the stacks are made up solely of TTF molecules and the halogen atoms are distributed in the channels between them[76].

The conductivities of $(DBTTF)Cl_{0.7-1.0}$ and $(DBTTF)Br_{0.8-1.0}$ were measured using discs and amount to $10^{-2}-10^{-3}$ Ω^{-1} cm^{-1}. The conduction in the $(DBTFF)I_3$ single crystals investigated [95] is activated and the magnetic susceptibility of this compound varies in accordance with the properties of an infinite antiferromagnetic chain having an exchange integral $J = 100$ K. [95]

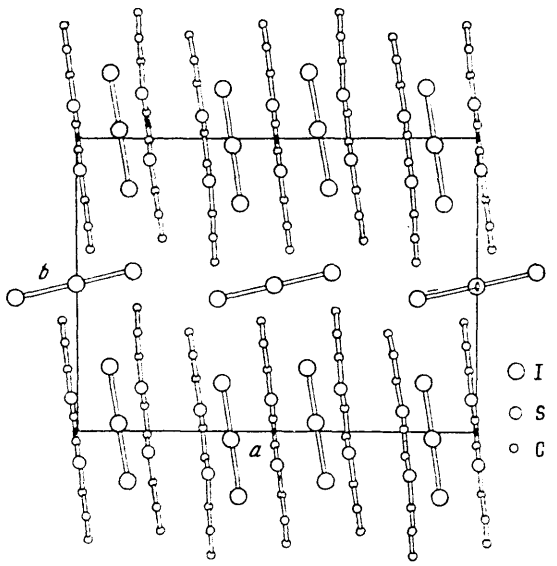


Figure 2. The structure of $(DBTTF)I_3$; [93] the side view of the DBTTF stacks with I_3^- anions accommodated in the channels between the stacks.

Metal halides and their complexes were used for the first time as oxidants for DBTTF. An interesting feature of these reactions is the fact that the oxidant behaves simultaneously as the complex forming anion or the anion can be formed in the course of the reaction[96,97]:

$$DBTTF + MX_4 \rightleftarrows DBTTF^+ + MX_3 + 2X^- \quad ;$$

$$MX_4 + 2X^- \rightleftarrows (MX_6)^{2-}$$

M=Sn, Te, X=Cl, Br

$$DBTTF + DBTTF^+ + (MX_6)^{2-} \xrightarrow{X=Cl} (DBTTF)_8(MCl_6)^{2-} \quad ;$$

$$DBTTF + DBTTF^+ + (MX_6)^{2-} \xrightarrow{X=Br} (DBTTF)_3(MBr_6)^{2-} \quad ;$$

M=Pt, Re, Sn, Te.

Table 3 presents the characteristics of the radical-ion salts obtained by oxidising DBTTF by various oxidants and the conductivities of the compounds obtained. The series of isostructural DBTTF compounds with doubly charged octahedral anions, having the general formula $(DBTTF)_8(MCl_6)_3^{2-}$, where M = Sn, Pt, Re, or Te, are of greatest interest. A characteristic feature of the structures of these compounds [97,98] is the presence of isolated cationic and anionic stacks arranged along the conducting axis of the crystal. Fig. 3 illustrates the lateral view of the cationic and anionic stacks in the $(DBTTF)_8(SnCl_6)_3$ structure. In the unit cell there are eight cations and three anions per period along the conducting axis of the crystal, the interplanar distance between the DBTTF molecules being identical throughout the stack and equal to 3.49 Å.

X-Ray diffraction study of the $(DBTTF)_8(MCl_6)_3$ complexes, where M = Sn, Pt, or Re, showed[98] that the presence of two sublattices—cationic with the single identical subperiod $c' = 3.49$ Å and anionic with the periods $c'' = 9.30$ Å for $SnCl_6^{2-}$,

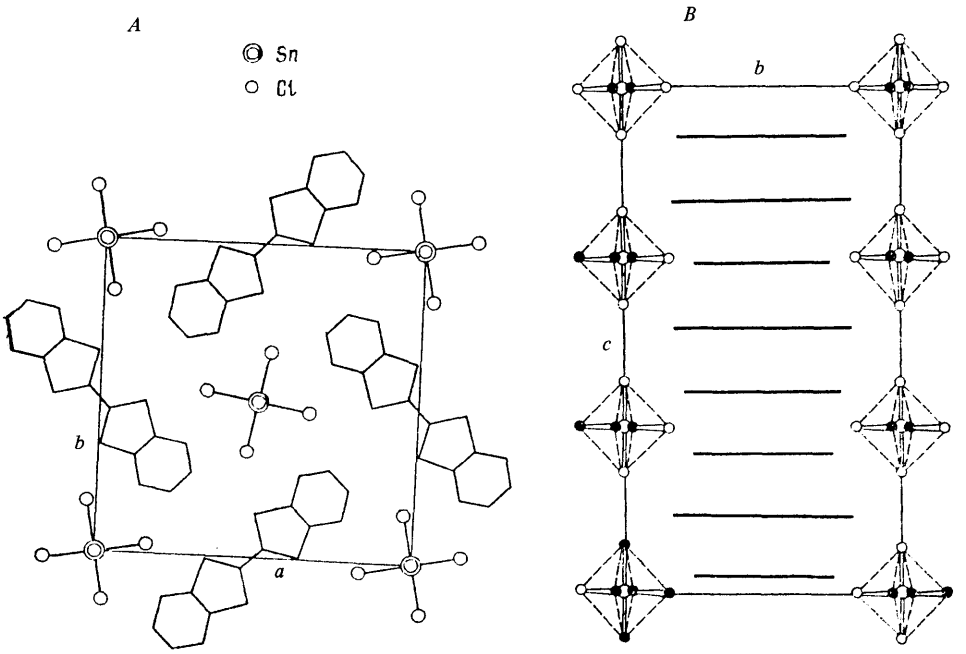


Figure 3. The structure of $(DBTTF)_8(SnCl_6)_3$; [98] *A*) view from above along the DBTTF stacks with the $SnCl_6^{2-}$ anion accommodated in the channels between the DBTTF molecules; *B*) side view of the cationic and anionic DBTTF and $SnCl_6^{2-}$ stacks.

9.52 Å for $PtCl_6^{2-}$, and 9.0 Å for $ReCl_6^{2-}$ —is manifested in the crystals of compounds of DBTTF with the MCl_6^{2-} anions. The ratios of the dimensions of the subperiods $c'':c'$ yield the ratios of the cationic and anionic components, which are 2.67:1, 2.73:1 and 2.59:1, and this also indicates the compositions of the complexes listed in Table 3. The small differences between the cationic components of these complexes, caused by the different dimensions of the octahedral anions which do not interact with one another, do not have a significant influence on the conductivities of the compounds. Conduction takes place via cationic stacks consisting of regularly arranged DBTTF molecules. In the compounds $(DBTTF)_8.(MCl_6)_3$ there are six radical-cation species and two neutral molecules for three doubly charged anions, so that the charge $(16-6):8=(10/8)e$ is formally localised on each molecule and the conductivity band is five-eights filled[99].

Table 3. Characteristics of the radical-ion salts of dibenzotetrathiofulvalene with inorganic anions.

Salt	σ, Ω^{-1} cm^{-1}	T_t, K	Refs.
$(DBTTF)Cl_{0.7-1.0}$	10^{-2}—10^{-3}	—	[91, 92]
$(DBTTF)Br_{0.8-1.0}$	10^{-3}—10^{-4}	—	[91]
$(DBTTF)Br_{1.2}$	10^{-1}	—	[72, 91]
$(DBTTF)I_3$	10^{-3} *	—	[91, 93]
$(DBTTF)_2I_3$	10^{-2}	—	[91]
(DBTTF)2I	10^{-3}	—	[94]
$(DBTTF)(BF_4)_{0.8}$	10^{-2}	—	[103]
$(DBTTF)_{2.5}FeCl_4$	40 *	—	[102]
$(DBTTF)_{2.6}SnCl_6$	300—500 *	115	[97, 99]
$(DBTTF)_{2.73}PtCl_6$	300—500 *	115	[97]
$(DBTTF)_{2.53}ReCl_6$	0.5—1.0	—	[101]
$(DBTTF)_8(TeCl_6)_3$	0.5—1.0	—	[100]
$(DBTTF)_3SnBr_6$	40 *	—	[97]
$(DBTTF)_3PtBr_6$	40 *	—	[97]
$(DBTTF)_3ReBr_6$	10^{-2}	—	[101]
$(DBTTF)S(CH_3)_2PtBr_5$	10^{-3} *	—	[101]
(DBTTF)CuCl3	10^{-7}	—	[96]
$(DBTTF)_2PF_6(THF)_{0.3}$**	0.1 *	240	[104]
$(DBTSF)(TaF_6)_{0.61}$	20 *	140	[37]
$(DBTSF)(AsF_6)_{0.67}$	3 *	—	[37]
$(DBTSF)(SbF_6)_{0.72}$	0,5 *	—	[37]

* Measured for a single crystal.
** THF = tetrahydrofuran.

Measurements of the temperature variation of the conductivities of $(DBTFF)_8(SnCl_6)_3$ and $(DBTTF)_8(PtCl_6)_3$ single crystals showed that σ increases somewhat with decrease of the temperature T (by a factor of approximately 1.5); this is followed by a broad maximum, after which at 180 K the conductivity begins to fall in accordance with an activation law and the salt passes to the dielectric state at 113–117 K.[99]

Measurements of the temperature dependence of the magnetic susceptibilities of the compounds $(DBTTF)_8(MCl_6)_3$, where M = Sn, Pt, Re, or Te, demonstrated a metal-dielectric phase transition at 115 K.[99,100]

The replacement of MCl_6^{2-} by the larger MBr_6^{2-} anions leads to a series of isostructural compounds having the general formula $(DBTTF)_3MBr_6$ (M = Sn, Pt, or Re). It has been shown for $(DBTTF)_3SnBr_6$[98] that the cationic stack is divided into triads with different distances between the DBTTF molecules, amounting to 3.47, 3.44, and 3.44 Å. The conductivities of the $(DBTTF)_3MBr_6$ complexes are lower by an order of magnitude than those of $(DBTTF)_8(MCl_6)_3$; for discs, $\sigma = 10^{-2}$ Ω^{-1} cm^{-1} for all the complexes, while for the single crystals of the compound $(DBTTF)SnBr_6$, we have $\sigma = 40$ Ω^{-1} cm^{-1} at 300 K.

The replacement of one Br^- ion in $PtBr_6^{2-}$ by the dimethyl sulphide group leads to the formation of the singly-charged anion $Br_5PtS(CH_3)_2^-$ and of the charge-transfer radical-cation salt $(DBTTF)[Br_5PtS(CH_3)_2]$, the conductivity of the single crystals of which is 10^{-3} Ω^{-1} cm^{-1}.[101]

The selenium analogue of dibenzotetrathiofulvalene, namely dibenzotetraselenofulvalene (DBTSF), has been obtained recently[37,46]. Its electrochemical oxidation in the presence of hexafluorophosphate anions leads[37] to the formation of the non-stoichiometric salts $(DBTSF)(TaF_6)_{0.61}$, $(DBTSF).(AsF_6)_{0.67}$, and $(DBTSF)(SbF_6)_{0.72}$ with single crystal conductivities of 0.5–20 Ω^{-1} cm^{-1} (Table 3). The properties of tetramethyldibenzotetraselenofulvalene (TMDBTSF), described by Johansen et al.[37], are of special interest in connection with the discovery of the superconductivity of TMTSF derivatives.

3. Organic Metals and Superconductors Based on Tetramethyltetraselenofulvalene

The greatest advance in the field of organic metals during the last three years has been the discovery of their superconductivity#.

The first organic superconductors were obtained in the form of 2:1 single crystal salts by the electrochemical oxidation of tetramethyltetraselenofulvalene in the presence of the corresponding tetra-alkylammonium salt[105,106,107]:

$$2TMTSF + (C_4H_9)_4X \xrightarrow[-e]{} (TMTSF)_2X.$$

The electrochemical method proved to be very suitable for the synthesis of single crystals of conducting compounds, because, during controlled oxidation or reduction by an electric current, the soluble donor or acceptor molecules are converted into less soluble oxidised or reduced complexes. The complexes of unsubstituted TTF,[80] TCQM[108], polycyclic aromatic compounds[54], and metal complexes of dithiolenes[109] have been obtained in this way. If electrochemical oxidation yields products with fairly high conductivities, they crystallise at the anode in the form of thin long needles or plates, since they can themselves function as the electrode, while the non-conducting compounds cover the anode in a thin film and electrocrystallisation stops.

The majority of organic metals are obtained nowadays by the electrochemical crystallisation method described by Mortensen and co-workers[105,110]. The purity of the initial electron-donating compounds, electrolytes, and solvents involved in the electrochemical process must meet very exacting requirements[105]. Special investigations of the influence of the donor purification conditions[110], the specific features of the solvents[111], and the construction of the electrochemical cell[112] on the quality of the crystalline salts formed have been carried out.

Chemical oxidation of TMTSF by copper(II) salts can yield (depending on the concentrations of the initial reactants and their ratio) salts having the compositions $(TMTSF)_2X$ or (TMTSF)X or the dicationic salts $(TMTSF)X_2$[82]:

$$TMTSF + CuX \rightarrow (TMTSF)_nX,$$
$$n = 2;\ 1;\ 0.5;\ X = BF_4,\ ClO_4,\ NO_3\ .$$

However, the resulting $(TMTSF)_2X$ crystals are then of a lower quality than in the electrochemical oxidation. Apart from the 2:1 salts, TMTSF salts of other compositions have

The properties of the superconducting salts $(DMTSF)_2X$ have been discussed in detail in "Proceedings of the International Conference on Low Dimensional Solids", Mol.Cryst. Liq.Cryst., 1982, **79**, Part II, 1–357.

been isolated[107]: $(TMTSF)Br_{0.8}$, $(TMTSF)(Br_3)_{0.8}$, $(TMTSF)_2(SiF_6)$, $(TMTSF)(TeF_5)$, and $(TMTSF)(R\text{-}SO_3)$, where R = *p*-tolyl or phenyl. The properties of compounds having other than 2:1 stoichiometry are those of semiconductors, while the salt $(TMTSF)_2(SiF_6)^{2-}$ is a dielectric[107].

Compounds having the composition $(TMTSF)_2X$, characterised by a wide range of variation of the physical properties from those of semiconductors to superconductors, are of greatest interest.

Table 4. Characteristics of the tetramethyltetraselenofulvalene salts $(TMTSF)_2X$.

Anion	σ^*, Ω^{-1} cm^{-1}	T_t, K	T_s, K	p_s, kbar	Refs.
ClO_4^-	400	***	1.4	****	[106, 107, 118]
ReO_4^-	400	180	1.3	9.5	[123]
BrO_4^-	300	200	***	***	[124, 130]
BF_4^-	540	40	**	12	[105, 107]
FSO_3^-	1600	86	3.5	6.5	[124—126]
NO_3^-	780	12	**	12	[105, 107]
$H_2F_3^-$	200	63	***	***	[127]
PF_6^-	540	12; 15	1.4	6.5; 8.5	[115, 117, 119, 121]
AsF_6^-	430	12; 15	1.4	9.5	[117, 132]
SbF_6^-	500	17	0.38	10.5	[117]
NbF_6^-	—	12	**	12	[117]
TaF_6^-	—	—	1.35	<11	[117]

Notation: T_t is the metal-dielectric transition temperature; T_S is the superconducting transition temperature; p_S is the pressure at which the compound undergoes the superconducting transition.

* At 300 K.
** There is no transition.
*** Not investigated.
**** At atmospheric pressure.

Table 4 presents the properties of the salts $(TMTSF)_2X$ with various singly-charged inorganic anions obtained hitherto. The anions present in these salts can be divided into the following groups in terms of their symmetry: octahedral (PF_6^-, AsF_6^-, NbF_6^-, SbF_6^-, TaF_6^-, TeF_6^-), tetrahedral symmetrical (BF_4^-, ClO_4^-, BrO_4^-, IO_4^-, ReO_4^-, and TcO_4^-), and tetrahedral asymmetric (FSO_3^- and $CF_3SO_3^-$); in addition there exist the triangular planar NO_3^- anion and the $H_2F_3^-$ anion. It is of interest to follow the differences between the compound $(TMTSF)_2X$ and other tetrathiofulvalene derivatives. All the compounds of the type $(TMTSF)_2X$ are isostructural. The almost planar TMTSF molecules are packed in stacks arranged exactly at right angles to the conducting axis of the crystal [146]. Fig. 4 [113] illustrates the structure of the compound $(TMTSF)_2ClO_4$, which is typical for the entire series of salts $(TMTSF)_2X$. Within the single stack, the molecules are arranged in a zigzag fashion with a shift equal to one quarter of the length of the molecule relative to one another (Fig. 4*a*, side view). Inside the stack, a weak dimerisation is observed: the distances between two neighbouring Se atoms of the TMTSF molecules in the stack are 4.021 and 3.96 Å; the distance between two other Se atoms are somewhat smaller (3.93 and 3.87 Å). A distinctive feature of these structures is the fact that the stacks are arranged in layers (Fig. 4*b*, view from above) with a very short Se-Se distance between the Se atom of neighbouring molecules in the layer, significantly smaller than the sum of the van der Waals radii of the Se atoms, which is 4.00 Å. [114] Such short Se-Se distances are responsible for the two-dimensional nature of this series of compounds (previously such shortened Se-Se distances between neighbouring stacks were found for the compounds TMTSF. .TCQM [115] and $(TST)_2Cl$). [31]

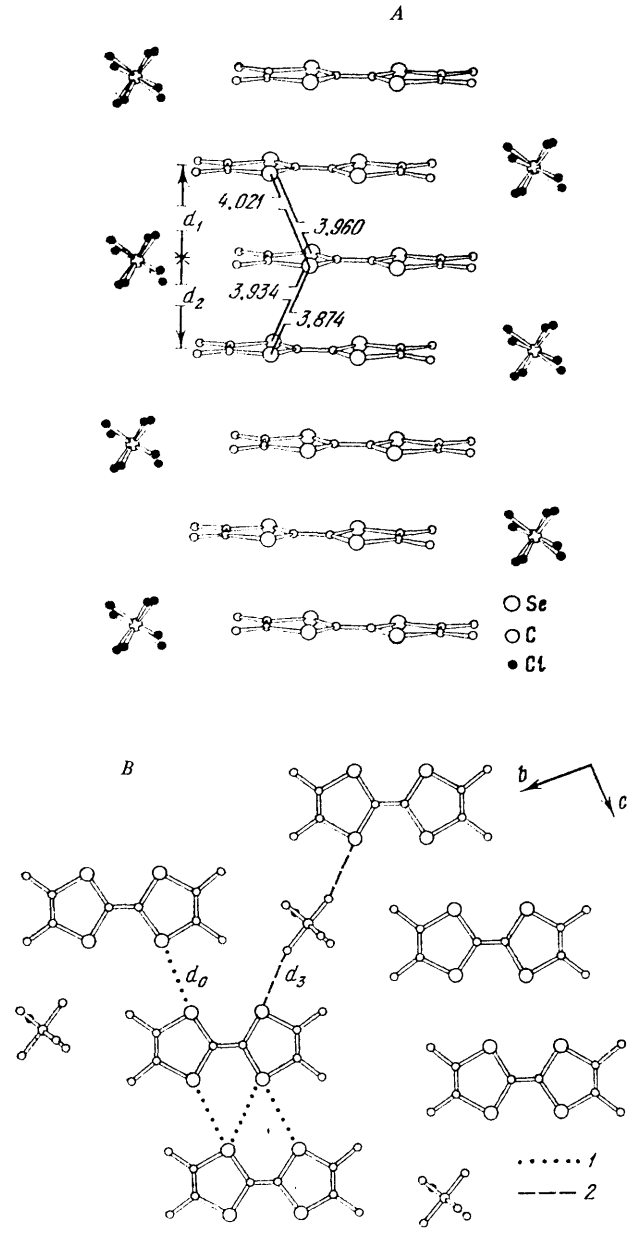


Figure 4. *A*) The structure of $(TMTSF)_2ClO_4$. [146] Side view of stacks of TMTSF molecules; the Se-Se distances between the TMTSF molecules within the stack are indicated; the ClO_4^- anions are located to one side; *B*) the structure of $(TMTSF)_2PF_6$; [113] the view from above the stacks of TMTSF molecules; the TMTSF molecules are evidently arranged in layers separated by PF_6^- anions; *1*) Se-Se distances in the layer of TMTSF molecules between individual stacks; *2*) Se-F distances.

Table 5. The distances between the stacks (d_0) of TMTSF molecules and within the stacks (d_1 and d_2) in $(TMTSF)_2X$ layers.

Anion	ClO_4^-		PF_6^-		AsF_6^-		ReO_4^-		FSO_3^-		$H_2F_3^-$		BrO_4^-		SbF_6^-	TaF_6^-
T, K	298 [146]	125 [116]	298 [113]	125 [116]	298 [132]	125 [116]	298 [123]	125 [123]	298 [125]	123 [125]	298 [127]	125 [127]	298 [124]	125 [124]	298 [117]	298 [117]
d_0, Å	3.77	3.655	3.88	3.741	3.90	3.789	3.827	3.70	3.866	3.829	3.816	3.735	3.875	—	—	—
d_1, Å	3.63	3.58	3.66	3.54	3.65	3.57	3.64	3.57	3.62	3.58	3.60	3.54	3.64	3.59	3.65	3.64
d_2, Å	3.62	3.57	3.63	3.59	3.62	3.57	—	—	3.63	3.57	3.60	3.53	—	—	—	—
d_3, Å	3.324	3.39	3.233	3.119	—	3.083	3.163	3.01	—	—	3.28	3.16	—	—	—	—
v_0, Å	694.3	673.7	714.3	681.3	719.9	698.3	710.5	—	695.3	677.7	671.2	650.0	707.2	689.8	737.0	735.6

Notation: d_3 is the minimum Se-O distance (in compounds with the ClO_4^- and BrO_4^- anions) or Se-F distance (for flourine-containing anions; v_0 is the volume of the unit cell; d_0 is the minimum Se-Se distance between TMTSF stacks in the layer; d_1 and d_2 are the interplanar spacings between TMTSF molecules within a single stack.

Note. The numbers in square brackets denote references (Ed. of Translation).

Table 5 lists the Se-Se distances in the stack and between the stacks for a series of salts $(TMTSF)_2X$. All these distances are significantly shorter than the sum of two van der Waals radii of the Se atom. For certain compounds (with PF_6^- and AsF_6^-), a weak dimerisation is observed within the TMTSF stacks ($d_2-d_1=0.03$ Å), but in the main the stacks are virtually not dimerised. With decrease of temperature, all the distances diminish, but the Se-Se distances between the stacks decrease much more than the Se-Se distances within the stacks (Table 5), i.e. the salts $(TMTSF)_2X$ become increasingly two-dimensional as the temperature is reduced[116].

Singly charged anions are arranged in the channels between the layers of TMTSF molecules; their arrangement is clearly seen from Fig. 4*b*. The centrosymmetric anions PF_6^-, AsF_6^-, SbF_6^-, TaF_6^-, and NbF_6^- can occupy only one position in the lattice[4,113,117]. The tetrahedral anions ClO_4^-, BF_4^-, ReO_4^-, BrO_4^-, SO_3F^-, etc., which lack central symmetry, can occupy two statistically non-equivalent positions in the lattice, which can vary with temperature. It has been suggested[117] that at low temperatures the ClO_4^- ions occupy only one position, but X-ray diffraction studies at 125 K [116] have shown that at least up to this temperature there is no ordering in the arrangement of the ClO_4^- ions. It has now been established that the differences between the structures of the anions and the changes occurring in their packing as the temperature is altered actually determine the entire wide variety of the properties of the salts $(TMTSF)_2X$.[4]

All the compounds of the $(TMTSF)_2X$ series have not unduly high electrical conductivities at room temperature, namely $\sigma \cong 400 \pm 100\ \Omega^{-1}\ cm^{-1}$ (Table 4), but, as the temperature is reduced, their conductivity increases very rapidly, reaching values of the order of $10^5\ \Omega^{-1}\ cm^{-1}$ for the majority of the salts before the transition temperature T_t.[107,119]

The salts of the octahedral anions (PF_6^-, AsF_6^-, SbF_6^-, TaF_6^-, and NbF_6^-) undergo the metal–dielectric transition at 12–17 K at normal pressures[107,117] (see Table 4). When an increased pressure is applied, the metal-dielectric transtion in compounds with the hexafluorophosphate anions is fully suppressed and all these compounds become superconducting at 0.9–1.3 K (Table 4).[117] It was shown for the first time in relation to the compound $(TMTSF)_2PF_6^-$ that the metal–dielectric transition is magnetic[120–122] and is associated with the antiferromagnetic ordering of the spins as the temperature is reduced with the formation of a spin density wave. The Peierls transition, which is usual for the organic metals investigated previously and is associated with a structural change in the conducting stack of organic molecules, is not observed for these compounds (the Peierls transition doubles the lattice period along the conducting axis of the crystal, which induces in its turn a periodic increase of the charge denisty along this axis, i.e. a charge density wave is generated[78]).

A different behaviour is characteristic of the salts $(TMTSF)_2X$ containing anions with a reduced symmetry (ClO_4^-, BF_4^-, ReO_4^-, NO_3^-, and FSO_3^-). At the usual pressure the salts $(TMTSF)_2ReO_4$,[123] $(TMTSF)_2FSO_3$,[124–126] and $(TMTSF)_2BF_4$,[105,107] undergo a sharp metal-dielectric phase transition at fairly high temperatures, namely at 180 K,[123] 86 K,[125] and 40 K[107] respectively (Table 4).

The metal-dielectric transition in the salt with the ReO_4^- anion has been attributed to the ordering of the arrangement of the ReO_4^- anions. At a pressure of 9.5 kbar the transition is suppressed and the compound undergoes the superconducting transition at 1.3 K.[123] It has been suggested that the metal–dielectric transition in systems with tetrahedral anions, similar to ReO_4^-, the behaviour of such systems under pressure and the influence of the position of the anion are associated with a special type of the Peierls mechanism which is based on the interaction of the conductivity electron with the ReO_4^- anion[123].

The salt $(TMTSF)_2FSO_3$ [125] differs from all other salts of this series by the fact that the FSO_3^- anion has a permanent dipole moment. The conductivity of the $(TMTSF)_2FSO_3$ single crystals[125] at 300 K is $\sigma = 1600\ \Omega^{-1}\ cm^{-1}$, which is higher than the usual conductivities of the series of $(TMTSF)_2X$ salts approximately by a factor of 4. With decrease of temperature to 86 K, a sharp metal–dielectric transition is observed and can also be noted in measurements of the magnetic susceptibility. It has been suggested[125] that the mechanism responsible for the metal-dielectric transition in this salt is associated with the generation of a charge density wave and not a

spin density wave. The physical properties of the salt are attributed to the influence of the permanent dipole moment of the FSO_3^- anion[125].

A qualtitatively different behaviour is characteristic of the compound $(TMTSF)_2NO_3$.[105,107] With decrease of temperature, the anions of this salt become ordered and the period of the unit cell is doubled along the conducting axis of the crystal.

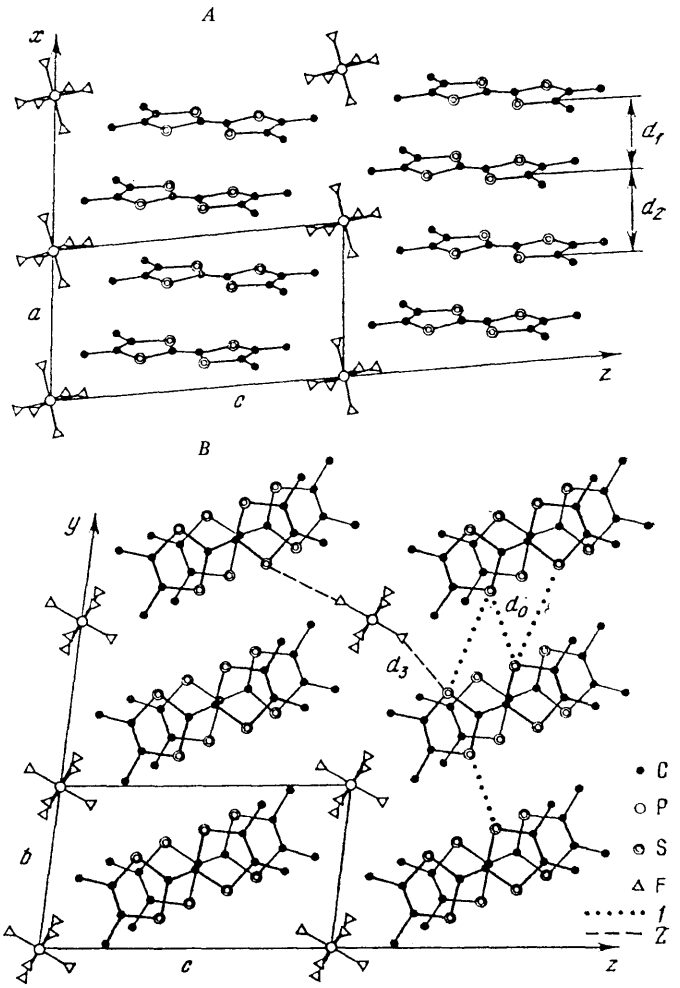


Figure 5. The structure of $(TMTTF)_2PF_6$: *A*) side view of the stacks of TMTTF molecules; the PF_6^- anions are distributed between the TMTTF stacks; *B*) view from above the layers of TMTTF molecules and PF_6^- anions; *1*) S–S distances between stacks of TMTTF molecules in the layer; *2*) S–F distances[135].

The order-disorder transition in the arrangement of the anions induces secondary effects in the electronic system of TMTSF. When pressure is applied, the metal-dielectric transition is suppressed, but the compound does not pass to the superconducting state. This is apparently associated with the fact that the NO_3^- anion is a relatively weak acceptor compared with the other anions investigated[107]. Yet another compound of the $(TMTSF)_2X$ series with the $H_2F_3^-$ anion has been obtained recently[127]. The $H_2F_3^-$ anion has a disordered arrangement and can occupy two possible positions around the centre of symmetry, each with a probability of 50%. This salt is isostructural with the other salts $(TMTSF)_2X$. Although the $(TMTSF)_2H_2F_3^-$ crystal has the smallest volume of the unit cell, the Se–Se distances in it are not the shortest (Table 5). The conductivity of this compound at room temperature is 200 Ω^{-1} cm^{-1}, but as the temperature is reduced, it undergoes the metal–dielectric transition (at 64 K).[127]

The salt $(TMTSF)_2ClO_4$ [105,107,118] is the only compound which does not undergo the metal–dielectric transition as the temperature is reduced and at 1.4 K at normal pressures it passes to the superconducting state. The principal difference between $(TMTSF)_2ClO_4$ and all other salts of this series is believed[106] to consist in the fact that the ClO_4^- ion has the smallest effective anionic radius. As a result of this, the interplanar spacings in the cationic stacks of $(TMTSF)_2ClO_4$ (Table 5) are smaller than in the other salts $(TMTSF)_2X$ under normal conditions and are close to the value which arises, for example, in $(TMTSF)_2PF_6$ under a pressure of 12 kbar.

The study of the resistivity[128] and elecronic heat capacity [129] of this salt as a function of the rate of cooling of the specimens showed a difference in its behaviour on rapid and slow cooling. The difference is associated with the fact that during rapid cooling the high-temperature disorder of the ClO_4^- anion persists and the length of the interchain linkage then diminshes[128,129].

The salts $(TMTSF)_2X$ with other anions, differing from those described in size (IO_4^- [110] and TcO_4^- [131]) and symmetry (TeF_5^- [107] and $CF_3SO_3^-$ [126]) are being investigated.

The main difference between $(TMTSF)_2X$ and all other compounds is the presence of layers of TMTSF molecules in them and shortened Se–Se distances between the stacks of individual TMTSF molecules, i.e. the presence of a definite degree of two-dimensional character. Since the interplanar spacings within the stack, d_1 and d_2 (Table 5), are ~3.6 Å (which is greater than the sum of two van der Waals radii of the carbon atom, equal to 3.4 Å),[114] one may conclude that electrical conduction takes place via short Se–Se contacts[132]. In the compounds $(TMTSF)_2X$, where $X = ClO_4^-$, PF_6^-, and AsF_6^-, the Se atoms are arranged in the stack at distances of 3.992, 4.005, and 3.992 Å respectively, while the corresponding distances between different stacks are 3.866, 3.924, and 3.988 Å (Table 5); thus the distances between the stacks are shorter by 0.05 Å (for AsF_6^-), 0.08 Å for (PF_6^-), and 0.126 Å (for ClO_4^-) than within the stack. It has been shown[116] that the structural changes occurring in the salts $(TMTSF)_2X$ on reduction of temperature are highly anistropic: the average distance between the stacks is shortened to a greater extent [116] (Table 5) (on average by a factor of between 1.6 and 2.1 for different anions) than the distances within the stack.

4. Organic Metals Based on Tetramethyltetrathiofulvalene

The observation of the metallic behaviour of the salts $(TMTSF)_2X$ down to low temperatures and of a transition to the superconducting state led investigators to turn to the S-analogues obtained previously[133,134], namely to salts of tetramethyltetrathiofulvalene (TMTTF) with various inorganic anions. Just as the elements S and Se show identical stoichiometries and structures, the structures of the salts $(TMTTF)_2Br$ and $(TMTTF)_2PF_6$ obtained previously[135] are identical with those of the salts $(TMTSF)_2X$; one could therefore expect that the study of the properties of the two series $(TMTSF)_2X$ and $(TMTTF)_2X$ with identical anions would help us to understand the causes of the similarities and differences

observed in the physical properties and to find real experimental parameters correlated with the superconductivity of the compounds. The study of sulphur derivatives has the advantage over the TMTSF salts that the synthesis of the initial compound TMTTF [42] is significantly simpler and does not involve the use of hydrogen selenide or carbon diselenide, which are difficult to obtain and are harmful. TMTTF salts are obtained either chemically[133,134] or electrochemically[136], similarly to the synthesis of TMTSF;[106] both procedures make it possible to obtain salts with the composition $(TMTTF)_2X$.

The oxidation of TMTTF by the halogens I_2, Br_2, and Cl_2 in solution in acetonitrile leads, like that of the unsubstituted TTF, to the formation of a large number of compounds of different compositions, whose conductivities vary within wide limits depending on the degree of charge transfer[133,134]:

Compound	σ, Ω^{-1} cm^{-1}	Compound	σ, Ω^{-1} cm^{-1}
$(TMTTF)_2I$	100	$(TMTTF)_2Br$	200
$(TMTTF)(I_3)_{0.45}$	50	$(TMTTF)Br_{0.8}$	100
$(TMTTF)I_3$	10^{-6}	$(TMTTF)(Br_3)_2$	—
		$(TMTTF)_2Cl$	10

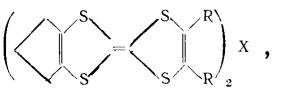
The individual TMTTF chlorides cannot be obtained by the direct oxidation of TMTTF with chlorine, but, using $SOCl_2$ as the oxidant, it is possible to isolate the chloride $(TMTTF)_2Cl$ [137] in the form of long thin needles (together with other reaction products).

By oxidising TMTTF with bivalent copper salts CuX_2 ($X = ClO_4$, BF_4, or NO_3), it is possible to obtain, as in the case of TTF and TMTSF,[82] three types of compounds depending on the reaction conditions (reactant ratio, concentration, and temperature): $(TMTTF)_2X$, $(TMTTF)X$, and $(TMTTF)X_2$.[82] The anion in CuX_2 must be capable of coordinating to Cu(I) less strongly than CH_3CN and be displaced by the latter from the coordination sphere of Cu(I).[81,82] Otherwise, TMTTF salts with a complex copper-containing anion are formed[138].

When TMTTF is oxidised by the inorganic salts $HgCl_2$,[139] $CuCl_2$,[138] and $MoCl_5$,[140] as for TTF and DBTTF,[96,97] an anion is formed, during the reaction in solution, whereupon crystals appear of both products with partial charge transfer of the type of $(TMTTF)_{1.25}Hg_2Cl_5^-$ with $\sigma = 10\ \Omega^{-1}$ cm^{-1} and $(TMTTF)_2CuCl_2$ with $\sigma = 1\ \Omega^{-1}$ cm^{-1} and compounds having the compositions $(TMTTF)HgCl_2$ and $(TMTTF)CuCl_3$ with $\sigma = 10^{-7}\ \Omega^{-1}$ cm^{-1}, in which complete charge transfer has taken place[138,139].

It is noteworthy that TMTTF complexes with partial charge transfer are, as it were, intermediates in the oxidation of TMTTF by inorganic salts and their isolation depends on the concentrations and ratio of the initial components. Thus, when TMTTF reacts with a 2.5-fold excess of $HgCl_2$ at the concentration $[TMTTF] = 2 \times 10^{-2}$ M, the radical-ion salt $(TMTTF)_{1.3}Hg_2Cl_5$ is formed; when the reactant ratio is smaller, the unreacted orange initial TMTTF is precipitated. Recrystallisation of $(TMTTF)_{1.3}Hg_2Cl_5$ from acetonitrile leads to further oxidation of TMTTF and the formation of the radical-ion salt $(TMTTF)(HgCl_3)$ and calomel. The interaction of TMTTF with $HgCl_2$ in dilute acetonitrile solutions at the concentration $[TMTTF] = 3 \times 10^{-1}$ M and the same reactant ratios does not lead to the product of the partial oxidation of TMTTF, the radical-cation salt $(TMTTF)HgCl_3$ being formed immediately and then crystallising in different modifications [139]. When TMTTF is oxidised by $CuCl_2$, the intermediate compound $(TMTTF)_2CuCl_2$ with partial charge transfer is formed and its formation is followed (possibly as a result of the catalytic oxidation of the $CuCl_2^-$ anion by atmospheric oxygen) by that of the anion $CuCl_3^-$ and of the corresponding radical-cation salt $(TMTTF)CuCl_3$, with complete charge transfer, in two modifications[138].

Preliminary studies of the salts of dimethyl-substituted TTF have shown that dimethyltetrathiofulvalene preferentially forms salts with inorganic anions having 2:1 or 1:1 compositions[110,147]. The conductivity of the latter is 50–300 Ω^{-1}cm^{-1} and there is a metal-dielectric transition at ~200 K. Asymmetric TTF derivatives also give rise to salts having the composition



where R = H or CH_3 and X are various fluorine-containing anions or ClO_4^-, [148,149].

From the standpoint of the study of physical properties, TMTTF salts having the composition $(TMTTF)_2X$ are of greatest interest, as for $(TMTSF)_2X$. The salts $(TMTTF)_2X$ are isostructural with the compound $(TMTSF)_2X$.[141] The degree of charge transfer in these salts, is determined, as for $(TMTSF)_2X$, by the valence state of the anion X^- and, for singly charged anions of the type BF_4^-, NO_3^-, PF_6^-, ClO_4^-, etc. the degree of charge transfer from each TMTTF and TMTSF molecule is 0.5; thus the conductivity band in $(TMTTF)_2X$ and $(TMTSF)_2X$ is three-quarters filled.

However, at normal pressures, the behaviour of the salts $(TMTTF)_2X$ differs from that of their selenium analogues[141]. Structurally the salts $(TMTTF)_2X$ are built up like the salts $(TMTSF)_2X$. The principal structural details can be seen in Fig.5, which represents the structure of the salt $(TMTTF)_2PF_6$.[135] Evidently here we have the same zigzag arrangement of the TMTTF molecules in the stack with a shift equivalent to one quarter of the length of the molecule along the conducting axis of the crystal (Fig.5*a*) and the stacks are arranged in individual layers (Fig.5*b*), while the PF_6^- anions are accommodated between layers of TMTTF molecules. However, the sulphur and selenium compounds differ significantly from one another in the distances between the individual molecular stacks in the layer.

In the salts $(TMTTF)_2X$ the interaction between neighbouring stacks in the layer can take place effectively via sulphur atoms in close proximity. Each TMTFF molecule has two sulphur atoms which are closest to the sulphur atoms of the next molecule. Table 6 presents the distances within the stack of TMTTF molecules (d_1 and d_2) and the S–S distances between neighbouring stacks. Evidently, these distances differ significantly for salts with different anions. The S–S distances within the stacks are not the same and differ slightly, i.e. the packing of the TMTTF molecules in the crystal is somewhat dimeric[136].

Table 6. Distances between TMTTF stacks (d_0) and within the TMTTF stacks (d_1 and d_2) for $(TMTTF)_2X$ salts[141].

Anion	Br^-	I^-	PF_6^-	ClO_4^-	BF_4^-	NO_3^-	SCN^-
d_0, Å	3.73	3.80	3.99	3.99	3.88	3.79	4.01
d_1, Å	3.53	3.54	3.62	3.59	3.56	3.56	3.56
d_2, Å	3.50	3.50	3.52	3.52	3.54	3.50	3.49
d_1-d_2, Å	0.03	0.04	0.10	0.07	0.02	0.06	0.07

All the interplanar spacings within the stack are less than the van der Waals radius of the sulphur atom, which is 3.6 Å. On the other hand, the S–S distances between the stacks are greater than 3.6 Å for all the salts $(TMTTF)_2X$ (Table 6).

Thus, these compounds are more one-dimensional than their selenium analogues. This is in fact responsible for the differences between the physical properties of the salts $(TMTSF)_2X$ and $(TMTTF)_2X$. The salt $(TMTTF)_2Br$, which has the smallest S–S distances and is least dimerised, is characterised by the highest conductivities among the series of compounds $(TMTTF)_2X$ (Table 7).

Table 7. Characteristics of the tetramethyltetrathiofulvalene salts $(TMTTF)_2X$ with different inorganic anions[136,141].

Anion	Cl^-	Br^-	I^-	PF_6^-	ClO_4^-	BF_4^-	NO_3^-	SCN^-
σ^*, Ω^{-1} cm^{-1}	10**	240	100	40	40	50	95	40
T_{max}, K	—	100	215	230	228	210	210	250
$\sigma_{max}/\sigma_{300}$	—	3.8	1.23	1.1	1.10	1.23	1.3	1.06
T_t, K	—	19	—	15	75; 10	41	160	—
T_t(K)/p(kbar)		24/25	10/30	30/30	—	—	—	—

Notation: T_{max} is the temperature at which the maximum conductivity of the specimen is observed; $\sigma max/\sigma_{300}$ K is the ratio of the maximum conductivity to the conductivity at room temperature; T_t is the metal-dielectric transition temperature; T_t/p is the temperature of the phase transition in the specimen at a pressure p.

* At 300 K.

** According to the data of Zhilyaeva et al[137].

The salts $(TMTTF)_2X$ have significantly lower conductivities at room temperatures ($\sigma = 40$–300 Ω^{-1} cm^{-1}) (Table 7) compared with the conductivities of the salts $(TMTSF)_2X$. When the temperature is reduced, the conductivity of $(TMTTF)_2X$ initially increases slightly (Table 7) up to 210–250 K and then begins to fall. An appreciable increase of conductivity (by a factor of 3.8) is observed only for $(TMTTF)_2Br$ and its decrease begins at 100 K.

Different types of behaviour, depending on the structure of the anion, are characteristic of the salts $(TMTTF)_2X$, as for $(TMTSF)_2X$.

The salt with the non-centrosymmetric anion SCN^- undergoes a sharp metal-dielectric transition at 160 K.[141] Some change in conductivity of $(TMTTF)_2ClO_4$ is observed at 75 K; this transition is manifested clearly in measurements of the magnetic susceptibility and heat capacity. The conductivity curves for the salts $(TMTTF)_2BF_4$ and $(TMTTF)_2NO_3$ show no distinct transitions but, in the measurement of the magnetic susceptibility and heat capacity of $(TMTTF)_2BF_4$, a transition is clearly shown at 40 K.[141]

It has been shown[142] that the phase transitions observed for all the salts $(TMTTF)_2X$ with tetrahedral anions are not of the Peierls type and are more probably associated with the ordering of the anionic sublattice, which is manifested in the study of various physical properties of these salts.

Among the salts with centrosymmetric anions, only $(TMTTF)_2Br$ shows a clear phase transition at 19 K, while the transition of $(TMTTF)_2PF_6$, determined from magnetic susceptibility measurements, is at 15 K.

A correlation has been found[141] between the conductivities of the salts $(TMTTF)_2X$ and the S–S distances for salts with different anions: $Br^- > NO_3^- > I^- > BF_4^- > ClO_4^- > PF_6^- > SCN^-$ (Tables 6 and 7).

The physical properties of the salts $(TMTTF)_2X$ change abruptly when pressure is applied. The conductivities of the salts $(TMTTF)_2BF_6$ and $(TMTTF)_2ClO_4$ increase sharply up to 10^5 Ω^{-1} cm^{-1} at pressures up to 30 kbar and the metal–dielectric transition is observed at the very low temperatures of 10 and 30 K respectively (Table 7). The metallic state of $(TMTTF)_2Br$ under pressure is stabilised down to the very lowest temperatures and its conductivity reaches 10^6 Ω^{-1} cm^{-1} before the metal-dielectric transition. The influence of pressure on the properties of $(TMTTF)_2Br$ is extremely complex. At 22 kbar the metallic state is stabilised down to 10 K, after which there is a transition to the dielectric state. The same specimen under a pressure of 25 kbar does not undergo the transition to the dielectric state and may pass to the superconducting state[136,141,142]. However, all these effects change very markedly from specimen to specimen; when the temperature is reduced, some of their crystals at atmospheric pressure exhibit an increase of conductivity by a factor of 400. These characteristics of the behaviour of the salt $(TMTTF)_2Br$ have been studied in detail[142].

The behaviour of the salts $(TMTTF)_2X$ after the application of pressure can be explained by their significantly greater one-dimensional character[141,142] compared with $(TMTSF)_2X$; the salts $(TMTTF)_2X$ therefore exhibit only under pressure the properties characteristic of the salts $(TMTSF)_2X$ at atmospheric pressure.

5. Organic Metals Based on Bis(ethylenedithiolo)tetrathiofulvalene

A report has been published recently on the synthesis of a new class of organic superconductors based on bis(ethylenedithiolo)tetrathiofulvalene (BEDT-TTF).[33] It had been stated earlier[47] that the radical-ion salt BEDT-TTF.TCQM has a very high conductivity ($\sigma = 40$ Ω^{-1} cm^{-1}) for a pressed specimen. The first salt of this electron donor with an inorganic anion was obtained[143] by the electrochemical oxidation of BEDT-TTF in methylene chloride and has the composition $(BEDT\text{-}TTF)_2ClO_4.0.5CH_2Cl_2$. Its conductivity at room temperature is 25–30 Ω^{-1} cm^{-1}; as the temperature is reduced, σ increases, reaching 1000 Ω^{-1} cm^{-1} at 16 K, and then diminishes slightly but remains high at the helium temperatures: $\sigma = 650$ Ω^{-1} cm^{-1} at 1.4 K.[143] The anisotropy of the conductivity of the specimen is $\sigma_\parallel/\sigma_\perp = 0.9$ at room temperature, diminishing somewhat (down to 0.4) at 3 K. This enabled the authors[143] to claim that the compound is dimeric, which has been confirmed by structural studies[144]. The distance between the BEDT-TTF molecules within the stack is fairly large, but the S–S distances between neighbouring stacks are extremely short, amounting to 3.3–3.45 Å (compared with the van der Waals radius of the sulphur atom of 3.6 Å), which is responsible for the highly two-dimensional character of this compound. The superconducting transition has not so far been observed for this compound, but its conductivity remains metallic down to 1.4 K. This is the first observation of the metallic properties of an electron-donating sulphur-containing compound down to such a low temperature[143].

BEDT-TTF salts with various inorganic anions have been obtained by the electrochemical oxidation of BEDT-TTF in tetrahydrofuran (THF);[33] the BEDT-TTF salts with the ReO_4^- anion exhibit the most interesting properties. Compounds of several compositions, namely the thin acicular crystals of $(BEDT\text{-}TTF)(ReO_4)_2.THF$ and the lamellar crystals of the two salts $(BEDT\text{-}TTF)_4(ReO_4)_2$ and $(BEDT\text{-}TTF)_5(ReO_4)_4$, whose composition does not include the solvent, were obtained in the course of electrochemical oxidation. All the salts obtained

have different conductivity properties. Among these compounds, the salt $(BEDT\text{-}TTF)_4(ReO_4)_2$ is a superconductor with the superconducting transition at 2 K and a pressure of 4 kbar. It is of interest that the structure of this salt is very similar to that of $(TMTTF)_2X$ and $(TMTSF)_2X$. The BEDT-TTF molecules are also arranged in a stack in a zigzag fashion along the conducting axis and form layers made up of BEDT-TTF molecules between which the ReO_4^- anions are accommodated. The S–S distance along the stack is significantly longer than between individual stacks in the layer. However, there are differences: (1) the methylene groups CH_2 are displaced from the plane of the main molecules; (2) the ReO_4^- anions are ordered at room temperature, in contrast to the salts $(TMTSF)_2ReO_4$ or $(TMTTF)_2ReO_4$. The conductivity of $(BEDT\text{-}TTF)_4(ReO_4)_2$ at room temperature and at the usual pressure is 200 Ω^{-1} cm^{-1}, while on decrease of temperature the metal-dielectric transition takes place.

Thus yet another class of organic superconductors based on a sulphur-containing electron donor has been discovered[33]. According to preliminary data, the selenium analogue bis-(ethylenediseleno)tetraselenofulvalene (BEDT-TTSF), obtained by the same authors[145], give rise to 1:1 salts as a result of the electrochemical reaction in the presence of the ReO_4^- and ClO_4^- anions, the conductivities of single crystal specimens amounting to 10^{-1}–10^{-2} Ω^{-1} cm^{-1}. The authors noted the very low solubility of BEDS-TSF and the difficulties in electrocrystallisation associated with this factor.

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The data described show that the compounds based on tetrathiofulvalene derivatives examined here can give rise to salts with a wide range of properties—from a dielectric to a superconductor. However, the metallic state characteristic of these salts over a certain range of temperature is frequently unstable and the metal–dielectric transition takes place. The main task, namely the preparation of an organic semiconductor or an organic metal stable down to the very lowest temperatures, is therefore still far from being solved.

Theory shows that the metallic state cannot be stabilised in a one-dimensional system. Quasi-one-dimensional systems with a certain amount of two-dimensional or three-dimensional character are necessary. The metallic state in such systems can be unstable in relation to the superconducting transition and the compound can become a superconductor under appropriate conditions.

As shown above, the amount of three-dimensional character in quasi-one-dimensional organic metals can be increased by applying pressure. This can lead in its turn to partial or complete suppression of the low-temperature transition to the dielectric state.

However, the greatest possibilities in this respect arise in synthetic chemistry. The introduction of four (and even two) methyl groups into the TTF molecule makes it possible to obtain qualitatively new compounds having the composition $(TMTTF)_2X$, differing in their structure from the non-stoichiometric compounds $(TTF)X_n$, for which the 2:1 composition cannot be obtained.

Simple replacement of the S atom by the Se atom in the TMTTF molecule makes it possible to increase the degree of interaction between the stacks in the quasi-one-dimensional metal, i.e. to increase the amount of two-dimensional or three-dimensional character of the compound without altering the structure of the compound as a whole. This is apparently the cause of the appearance of superconductivity following the application of pressure to the salts $(TMTSF)_2X$, where $X = PF_6^-$, AsF_6^-, TaF_6^-, SbF_6^-, ReO_4^-, or FSO_3^-, while the compound $(TMTSF)_2ClO_4$ undergoes the superconducting transition at 1.4 K even at atmospheric pressure.

The increase of the number of sulphur atoms in the structure of the cation made possible in its turn the synthesis of the first superconductor based on a sulphur-containing donor: $(BEDT\text{-}TTF)_4(ReO_4)_2$.

By selecting the appropriate anion, it is possible to vary widely the physical properties in a single series of compounds. In conformity with the correlation found[131] between the unit cell parameters and the superconducting properties of the salts $(TMTSF)_2X$, it has been suggested that the salts of TMTSF with the POF_2^- anion or with the mixed anions ClO_4^-–BF_4^-, etc. may have properties closest to those of the superconducting salt $(TMTSF)_2ClO_4$.

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