Organic Conductors with Unusual Band Fillings

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Contents

1. Introduction

Most organic superconductors have 2:1 composition as represented by (TMTSF)$_2$X and (ET)$_2$X (TMTSF = tetramethyltetraselenafulvalene and ET = bis-(ethylenedithio)tetrathiafulvalene), and since X is a 1− anion, the donor molecule has a 1/2+ charge.[1,2] Because the HOMO (highest occupied molecular orbital) of a donor molecule can contain up to two electrons (or holes), the 1/2+ charge corresponds to quarter filling; three-quarters of the HOMO energy band is occupied by electrons, and the remaining one-quarter is empty. The quarter filling seems to be an important requisite of the existing theory of organic superconductors, in particular of the universal phase diagrams of quasi-one-dimensional (TMTSF)$_2$X series and two-dimensional κ-phase (ET)$_2$X salts.[3,4] According to the universal phase diagrams, the superconducting phase is believed to appear on the boundary between an antiferromagnetic insulating phase and a metallic phase. There are, however, a few organic superconductors that have composition other than

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2:1. These unusual superconductors are less understood and are a benchmark to examine our understanding of organic superconductors. In addition, several 1:1-composition organic metals such as (TTM-TTP)I$_3$ and (DMTSA)BF$_4$ have been investigated,[5,6] and organic metals with other fractional band fillings have been explored (TTM-TTP = 2,5-bis(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene and DMTSA = 2,3-dimethyltetraselenoanthracene).[7,8] Recently, a series of organic superconductors with nonstoichiometric composition, represented by (MDT-TSF)(AuI$_2$)$_{0.436}$ (MDT-TSF = methylenedithiotetraselenafulvalene), have been obtained.[9,10] In the case of organic conductors, usually we cannot change the composition continuously, but we obtain a compound with a definite noninteger composition. Then we will use "nonstoichiometric" as the meaning of the noninteger composition.

TMTSF　　ET (BEDT-TTF)　　MDT-TSF

TTM-TTP

DMTSA
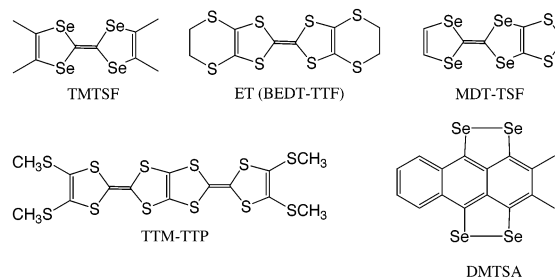
The purpose of the present review is to provide a comprehensive survey of these organic conductors with unusual band fillings. A systematic study of usual organic conductors has been reported previously.[11–13] This review is mainly intended to describe the basic structural and physical properties of highly conducting materials. Compilation of relatively low conducting materials is not attempted, though some related compounds, particularly ET salts with high oxidation states, are described. Although the degree of charge transfer is noninteger in such donor−acceptor complexes as (NMP)(TCNQ) and (TTF)(TCNQ), these kinds of charge-transfer complexes are not discussed in this review (NMP = N-methylphenadinium, TCNQ = tetracyanoquinodimethane, and TTF = tetrathiafulvalene).[14] There
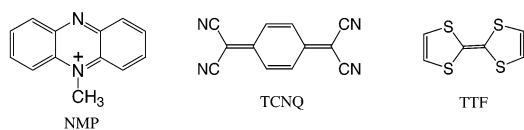
are a large number of nonstoichiometric halogenated compounds such as $(TTF)X_x$ and (metal phthalocyanine)I_x, which have been compiled in the review of Marks and Kalina.[15] KCP ($K_2[Pt(CN)_4]Br_{0.3}\cdot3H_2O$) and the related platinum complexes are also within this category,[16] but they are not dealt with in this review. A number of nonstoichiometric charge-transfer compounds have been reported on the basis of chemical analysis. This review is limited to compounds that have been characterized by single-crystal X-ray diffraction data.

2. Standard Model of Organic Superconductors

Before the individual compounds are described, it may be instructive to summarize what is believed in the usual organic conductors. Figure 1 illustrates
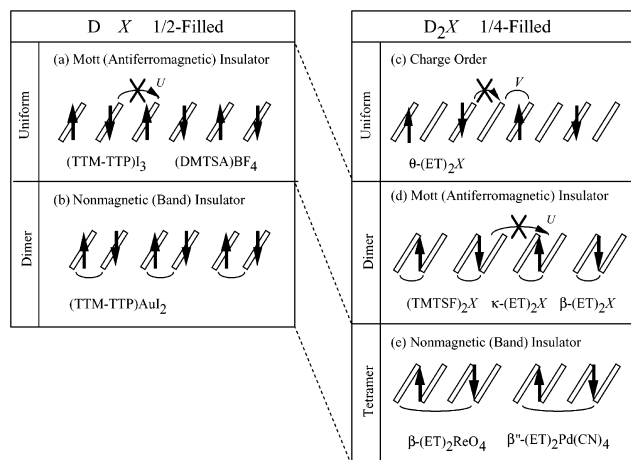

Figure 1. Relation of band filling and the lattice periodicity.

various situations in half and quarter fillings. Figure 1 is depicted for one-dimensional chains, but the following discussion applies more appropriately to multidimensional systems.

If only the band theory is considered, all compounds with partially filled bands are metals. This

is not true when the Coulomb repulsion between electrons works. If a uniform chain is half-filled (Figure 1a), each molecule has one electron, and the electron cannot move unless some molecule contains two electrons at a certain moment. This situation has higher energy than the ground state by U, which is the on-site Coulomb repulsion between the two electrons occupied on the same molecule at the same time. The model including U is called the Hubbard model.[17] The exact solution of the one-dimensional Hubbard model tells us that this one-dimensional chain is insulating for all non-zero U,[18] but the more naive mean-field theory appropriate for multidimensional cases demonstrates that the system becomes insulating approximately above $U > W$, where W is the bandwidth.[19] This type of insulator that is induced by U is called the Mott insulator[20] and is paramagnetic in the insulating phase, which sometimes undergoes an antiferromagnetic transition at low temperatures. When the chain is dimerized as in Figure 1b, two electrons in a dimer make a singlet state, and if the dimerization is sufficiently strong, the system falls into a nonmagnetic insulating state. In other words, this situation is regarded as a band insulating state derived from the uniform state in Figure 1a by the Peierls distortion.

From the Hubbard model, all band fillings other than the half filling are metals, and the Mott insulating state occurs only in the half filling.[21] Accordingly, a quarter-filled uniform state designated in Figure 1c is expected to be a typical metal. However, some of the actual quarter-filled uniform systems are insulators. This happens if the off-site Coulomb repulsion V between the electrons located on the adjacent molecules is taken into account. When an electron moves on the adjacent molecule, the energy increases by V, so that electrons are localized on every other molecule. In the case of holes, the donor molecules have such charges as $D^+D^0D^+D^0D^+D^0$. This insulating state is called charge order or charge separation. Since the θ-phase is a good example of a two-dimensional uniform structure, charge order in the θ-phase has been studied extensively.[22] In the metal−insulator transitions of the θ-phase, which are induced by the charge order, the transition temperature rises with increasing dihedral angle of the donor molecules on the adjacent stacks.[12,23] This rule is known as the universal phase diagram of the θ-phase. Since the charge order breaks the equivalence of the uniform molecules, some kind of symmetry lowering has to accompany the insulating state of the quarter-filled uniform states. Recently, a quarter-filled insulating state without lattice distortion has been reported in (EDT-TTF-CONMe$_2$)$_2$-AsF$_6$,[24] though the origin of the insulating state is still not resolved (EDT-TTF-CONMe$_2$ = dimethyl-carboamidoethylenedithiotetrathiafulvalene).
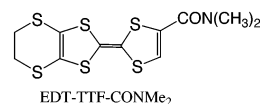
Another mechanism to make a quarter-filled uniform phase insulating is the lattice distortion. The
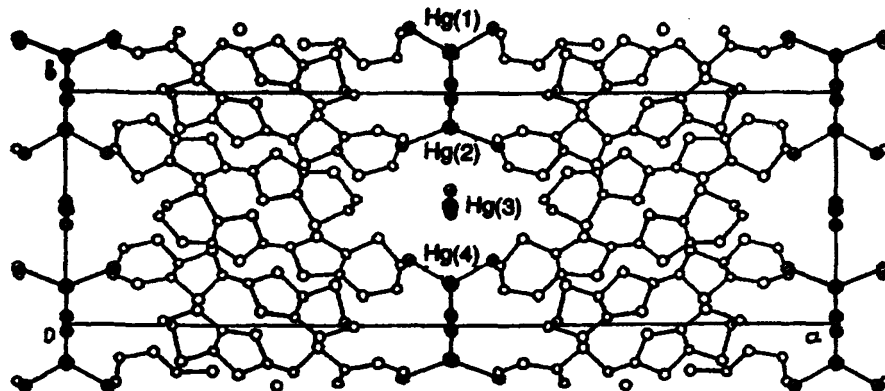
Figure 2. Crystal structure of κ-(d_8-ET)4Hg$_3$Br$_8$, projection onto the *ab* plane. Reprinted with permission from ref 36. Copyright 1993 EDS Sciences.

dimerized lattice in Figure 1d realizes a situation in which each dimer has one electron. If the dimerization is sufficiently strong, this is equivalent to the uniform half filling in Figure 1a, and the Mott insulating state is achieved. The two-site Hubbard model applies to this strongly dimerized situation, in which U is replaced by the degree of dimerization $2t$ (t is the intradimer transfer integral).[4,25] The system transforms from a metal to a Mott insulator when $2t$ increases or W decreases. It is believed that superconductivity appears on this boundary, as represented by the universal phase diagram of the two-dimensional κ-phase (ET)$_2$X salts.[3,4] Most organic superconductors are explained from this "quarter-filled dimerized" band.

If the tetramerization is sufficiently strong, as shown in Figure 1e, a nonmagnetic insulating state is possible similarly to that in Figure 1b. In one dimension, this corresponds to the $2k_F$ charge density wave (or Peierls) state, whereas Figure 1d may be regarded as the $4k_F$ charge density wave state.

3. Conductors Slightly Deviated from the Quarter Filling

Although most organic superconductors fall into the category of Figure 1d, there are a few exceptions that are not quarter filling. A slight deviation from the quarter filling has been claimed for κ-(ET)$_4$Hg$_{3-\delta}$X$_8$ (X = Cl and Br) and κ-(ET)$_2$Cu$_2$(CN)$_3$.

### 3.1. κ-(ET)$_4$Hg$_{3-\delta}$X$_8$ (X = Cl and Br)

A large number of mercury halide salts of ET have been reported,[26] but these κ-salts are prepared under the special conditions of the electrocrystallization, in which HgX$_2$ is added together with Bu$_4$NHgX$_3$ in the solvent (tetrahydrofuran (THF) or 1,1,2-trichloroethane).[27] The anion part consists of two edge-shared HgX$_4$ tetrahedra (Hg$_2$X$_6{}^{2-}$) and a quasi-linear HgX$_2$ molecule (Figure 2).[28-30] The Hg$_2$X$_6{}^{2-}$ unit and the HgX$_2$ unit are arranged alternately, so that the ideal composition is κ-(ET)$_4$Hg$_3$X$_8$. The thermal ellipsoids of the Hg atoms are, however, anomalously elongated along the anion chain. In addition, a superlattice originating from the Hg atoms appears along this anion chain. From the lattice constant of the super-

lattice (for example, 3.877 Å for the Br salt), which corresponds to the average Hg−Hg spacing, together with that of the donor lattice (11.219 Å), the composition is evaluated as 11.219/3.877 = 2.89, namely as κ-(ET)$_4$Hg$_{2.89}$Br$_8$,[26,30] and similarly as κ-(ET)$_4$Hg$_{2.78}$Cl$_8$.[26,28] Since the idealized Hg$_3$X$_8$ unit should have a 2− charge, the donor charge is slightly larger than 1/2+ (0.5 + δ/2). The estimation from the infrared C=C stretching modes also suggests a slightly larger value than the quarter filling (0.554+ for the Cl salt).[31]

The Br salt is an ambient-pressure superconductor at T_c = 4.3 K,[32] with pronounced two-dimensional anisotropy,[33] and the critical field ($B_{c2\parallel}$ = 14 T at 1.5 K) is reported to largely exceed the Clogston limit.[34] Although T_c of usual organic superconductors decreases under pressure, this compound shows an unusual increase of T_c. It increases up to 6.7 K under the pressure of 3.5 kbar.[35] The Cl salt shows practically metallic conductivity down to low temperatures but is superconducting only above 12 kbar at 1.8 K.[28] The transition temperature rises to 5.4 K at 29 kbar, but only partial superconductivity has been observed.[36] The deuterated Br salt, κ-(d_8-ET)$_4$Hg$_3$Br$_8$, does not exhibit superconductivity at ambient pressure but is superconducting only under a pressure of 0.3 kbar at T_c = 3.0 K.[30,36-38] This is, however, attributed to the use of Hg(NO$_3$)$_2$ instead of HgBr$_2$ as additional reagent in the electrocrystallization. The crystal structure of the deuterated Br salt is described in detail,[30] but the superlattice is not discussed. The optical reflectance spectra of the Cl and the Br salts are similar to those of other κ-phase (ET)$_2$X salts.[38] The electron spin resonance (ESR) and the static susceptibility measurements show Bonner−Fischer-type susceptibility (J = −74 K for the Cl salt).[39] The temperature dependence of thermoelectric power is linear at high temperatures but changes sign, and it is not linear at low temperatures.[39] The ^{1}H NMR $T_1{}^{-1}$ is reported to be anomalously frequency dependent for the Br salt, probably due to cross-relaxation via quadrupolar Br, and does not follow the simple Korringa relation both for the Cl and for the Br salts.[40] The detailed geometry and the transfer integrals of these κ-(ET)$_4$Hg$_{3-\delta}$X$_8$ salts are discussed to be much different from those of the standard κ-salts.[12]

The iodide salt, $(ET)_4Hg_3I_8$, has basically the same anion structure, but the donor arrangement is probably different (α-type).[41] The anion structure of this compound is described as an infinite chain of edge-shared HgI_4 tetrahedra. Then the composition is $(ET)_4Hg_3I_8$ and has no Hg deficiency. The Hg sites are, however, occupied by 50% probability, and another 50% are placed on every midpoint of adjacent Hg sites. The resulting quasi-linear chain of Hg is practically the same as that described in κ-$(ET)_4Hg_{2.98}Br_8$, though a superlattice is not reported in the iodine salt. Its temperature dependence of the resistivity is flat down to 260 K, at which an abrupt metal−insulator (MI) transition takes place. This abrupt transition has a large influence on ESR and the optical properties.[42]

Many salts with the same composition, $(D)_4Hg_3X_8$, are reported, where D is a donor molecule different from ET.[43] Among them, κ-$(BETS)_4Hg_{2.84}Br_8$ is superconducting below 3 K (BETS = bis(ethylenedithio)tetraselenafulvalene).[44] Recently, $(EDT-TTF)_4$-$Hg_{3-\delta}I_8$ is reported to be superconducting at $T_c = 8.1$ K under a pressure of 0.3 kbar (EDT-TTF = ethylenedithiotetrathiafulvalene). The structure of this compound is not known, and δ is determined to be 0.1−0.2 from electron probe microanalysis (EPMA).[45]

BETS   EDT-TTF
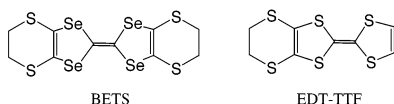
These $(D)_4Hg_{3-\delta}X_8$-type materials are interesting superconductors, but the conducting behavior varies from sample to sample. Besides the superlattice detection, experimental methods that determine the degree of charge transfer, particularly the observation of the Shubnikov−de Haas oscillation, are not reported.

3.2. κ-$(ET)_2Cu_2(CN)_3$

This is a family of κ-phase $(ET)_2X$ salts which give the highest T_c among organic superconductors.[1,2] The Argonne group has reported that κ-$(ET)_2Cu_2(CN)_3$ is superconducting only under a pressure of 1.5 kbar at $T_c = 2.8$ K.[46] The Kyoto group has, however, found that κ'-$(ET)_2Cu_2(CN)_3$, which is prepared in the presence of $N(CN)_2^-$ together with CN^-, is superconducting at 4.1 K at ambient pressure.[47] Komatsu et al. have attributed this difference to the incorporation of about 0.1% Cu^{2+} in the κ'-salt.[48] Then the band filling control is responsible for the ambient-pressure superconductivity. From the infrared spectra, however, Drozdova et al. have concluded that the anion layer of the κ'-salt is a mixture of $Cu_2(CN)_3$ and $Cu[N(CN)_2]CN$, and the $Cu[N(CN)_2]CN$ part gives rise to the ambient-pressure superconductivity.[49] Also for κ-$(BETS)_2Cu_2(CN)_3$, the influence of anion disorder is claimed, and the absence of a valence mixing of copper is concluded.[50] The interest in κ-$(ET)_2Cu_2(CN)_3$ is recently refreshed because this particular compound is reported to be described by a triangular lattice.[51]

4. Stoichiometric Band Fillings Other than Quarter Filling

4.1. ET Salts with Nonmetal Anions

Table 1 shows non-2:1 ET salts with nonmetal anions. The 3:2 salts with a composition like

Table 1. Non-Quarter-Filled ET Salts with Nonmetal Anions

compound[a]	conductivity[b]	structure	ref
0.6+			
$(ET)_5Cl_3(H_2O)_5$	$T_{MI} = 160$ K		52
2/3+			
$(ET)_3(FSO_3)_2$		β''	53
$(ET)_3(HSO_4)_2$		β''	53
$(ET)_3(BF_4)_2$	$T_{MI} = 150$ K	β''	54
$(ET)_3(ClO_4)_2$	$T_{MI} = 170$ K	β''	55
$(ET)_3(BrO_4)_2$	$T_{MI} = 210$ K	β''	56
α-$(ET)_3(NO_3)_2$	$T_{MI} = 20$ K	β''	57
$(ET)_3(IO_4)_2$	I	β''	58
$(ET)_3Cl_2(H_2O)_2$	$T_{MI} = 100$ K	β''	59, 60
	$T_{SC} = 2$ K (16 kbar)		
$(ET)_3Br_2(H_2O)_2$	$T_{MI} = 185$ K	β''	61
$(ET)_3Br_2(H_2O)_2$	$T_{MI} = 80$ K	β''	62
1+			
$(ET)Br$	I	dimer	63
$(ET)IO_4(THF)_{0.5}$	I	dimer	64
$(ET)PF_6$	I (10^{-3} S cm^{-1})		65
δ-$(ET)PF_6$		dimer	66
ϵ-$(ET)PF_6$			67
$(ET)PF_6(C_2H_2Cl_2)_{0.5}$		dimer	68
2+			
$(ET)(ClO_4)_2$	I		69
$(ET)(BF_4)_2$	I		69

^{a} THF = tetrahydrofuran. ^{b} I = insulators at room temperature and RT conductivity.

$(ET)_3(ClO_4)_2$ are common in small anions such as ClO_4.[55] All of these 3:2 salts are β''-type phase.[11] The conductivity is weakly metallic around room temperature and undergoes a sharp metal−insulator (MI) transition at low temperatures.

A considerable number of Cl and Br salts of ET have been reported.[62] Although many of them are 2:1 salts, $(ET)_3Cl_2(H_2O)_2$ is an exceptional member of the 3:2 salt family.[59,60] This compound is easily obtained in many different ways. For example, if ET is electrolyzed in the presence of unusual inorganic or organic anions that are not included in the ET salt in a Cl-containing solvent (e.g. 1,1,2-trichloroethane), some Cl is extracted from the solvent, and this complex is obtained. Although the other 3:2 salts include three donor molecules in a unit cell, this salt contains six ET molecules, and the anion unit is $Cl_4(H_2O)_4$, where Cl and O atoms are hydrogen bonded (Figure 3). This compound exhibits a comparatively high room-temperature conductivity of 500 S cm^{-1} as an ET salt, and the temperature dependence is weakly metallic down to 100 K, below which a nonmagnetic insulating state appears (Figure 4).[70] The MI transition is suppressed under pressure, and a superconducting phase appears under a pressure of 16 kbar at $T_c = 2$ K (Figure 5).[71,72] The band structure is semimetallic, as in other β''-type salts (Figure 6).[59] The small pockets due to the semimetallic band structure have been detected by the Shubnikov−de Haas experiments.[73] This is a repre-
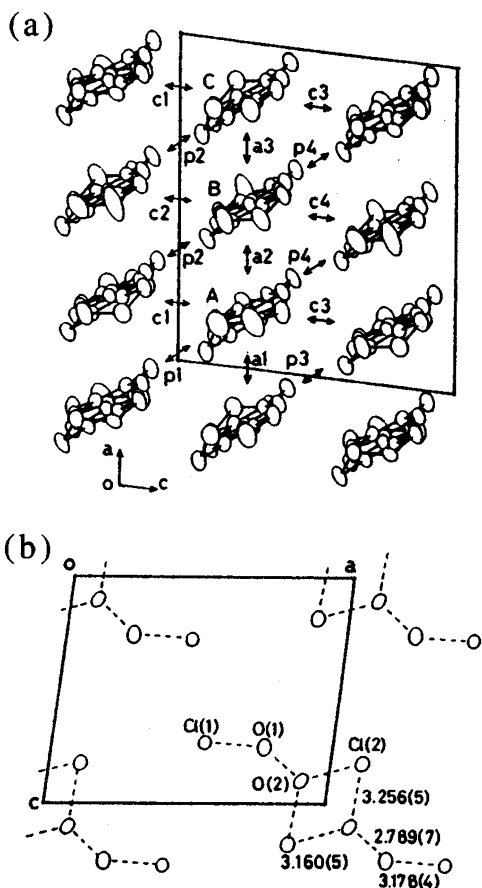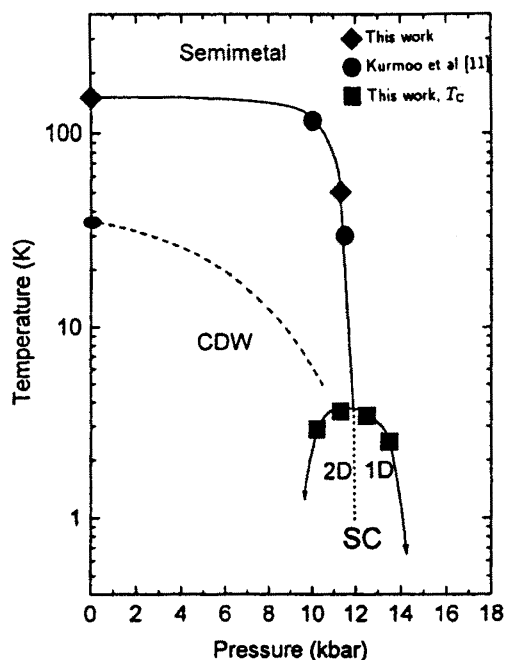
Figure 3. Crystal structure of $(ET)_3Cl_2(H_2O)_2$: (a) the donor arrangement; (b) the anion structure. Reprinted with permission from ref 59. Copyright 1987 The Chemical Society of Japan.
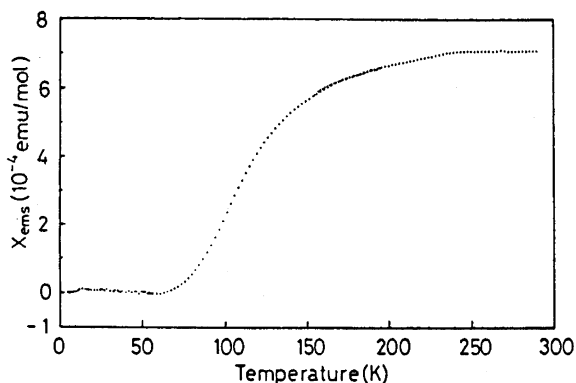
**Figure 4.** Static magnetic susceptibility of $(ET)_3Cl_2(H_2O)_2$. Reprinted with permission from ref 70. Copyright 1990 Springer Verlag.

sentative compound in which a nonmagnetic insulating phase borders the superconducting phase.[13] In general, β''-type superconductors such as β''-$(ET)_2Pt$-$(CN)_4H_2O$ and β''-$(ET)_2Pd(CN)_4H_2O$ border nonmagnetic insulating states.[13,74] The first ET-based superconductor, β-$(ET)_2ReO_4$, also has a nonmagnetic ground state at ambient pressure.[75]

As shown in Table 1, there are several 1+ salts, but these are strongly dimeric. As a consequence, these salts are highly insulating. Dicationic salts of ET, for example, $(ET)(ClO_4)_2$ and $(ET)(BF_4)_2$, have been prepared by using a mixed solvent of 10% CS_2 in $ClCH_2COCl$.[69]

Figure 5. Phase diagram of $(ET)_3Cl_2(H_2O)_2$. Reprinted with permission from ref 72. Copyright 2002 Institute of Physics and IOP Publishing.
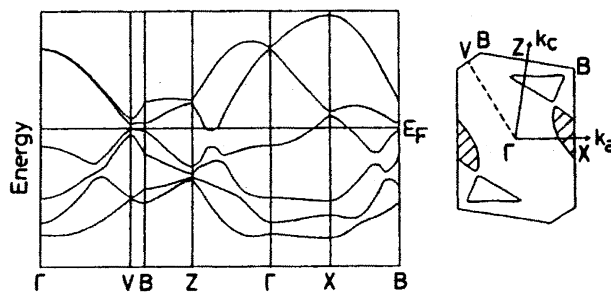
Figure 6. Band structure of $(ET)_3Cl_2(H_2O)_2$. Reprinted with permission from ref 59. Copyright 1987 The Chemical Society of Japan.

Since many salts with various degrees of charge transfer are obtained, it is important to estimate the donor charges. For such typical donor molecules as TTF and ET, we can estimate the donor charge from the bond lengths.[69,76,77] The change of the central C=C distance ($\Delta d = 0.13$ Å from D^0 to D^{2+}) is larger than that of the next C—S bond ($\Delta d = 0.07$ Å).[69] Then it is usually most convenient to compare the central C=C distance, but the comparison of the average of four of the next C—S bonds helps the estimation.

The charge is also estimated from C=C stretching of the Raman spectra.[31] Wang et al. have proposed that the two Raman modes ν_3 and ν_4 are obtained as linear functions of the donor charge Z as follows:

$$\nu_3\,(\text{cm}^{-1}) = -Z \times 86.0 + 1539$$

$$\nu_4\,(\text{cm}^{-1}) = -Z \times 88.4 + 1508$$

From these equations, the donor charge Z can be estimated.

In addition to the well-known quarter-filled α- and β-phases, there are a considerable number of ET iodine salts; these phases are summarized in Table

Table 2. Iodine Salts of ET

compound	synthetic method[a]	I/ET	charge	conductivity[b]	ref
α-(ET)$_2$I$_3$	E/THF	1.5	1/2+	T_{MI} = 135 K	78
β-(ET)$_2$I$_3$	E/TCE	1.5	1/2+	T_{SC} = 1.5 K (8 K)	79
θ-(ET)$_2$I$_3$	E	1.5	1/2+	T_{SC} = 3.6 K	80
κ-(ET)$_2$I$_3$	E/THF	1.5	1/2+	T_{SC} = 3.6 K	81
γ-(ET)$_3$(I$_3$)$_{2.5}$	E	2.5	5/6+	T_{SC} = 2.5 K	82
δ-(ET)$_3$I$_3$(TCE)$_{0.33}$	E/TCE	3	1+	T_{MI} = 160 K	83
η-(ET)I$_3$	D/PhCN	3	1+	I (10^{-4} S cm^{-1})	84
ϵ-(ET)$_2$I$_3$(I$_8$)$_{0.5}$	D/PhCN	3.5	1+	I	85
λ-(ET)$_2$I$_3$I$_5$	DV/PhCN	4	1+	I	86
ζ-(ET)$_2$I$_2$I$_8$	D/PhCN	5	1+	I	87

[a] E = electrochemical crystallization. D = direct reaction of ET with iodine in solution. DV = direct reaction of ET solution with iodine vapor. TCE = 1,1,2-trichloroethane. [b] I = insulators at room temperature and RT conductivity.

2 in increasing order of the iodine content. The donor sheet of γ-(ET)$_3$(I$_3$)$_{2.5}$ consists of ET trimer and two I$_3^-$ anions as (ET)$_3$(I$_3$)$_2$, while the remaining (I$_3^-$)$_{0.5}$ forms the anion sheet.[82] In δ-(ET)$_3$I$_3$(TCE)$_{0.33}$, half of the I$_3^-$ is incorporated in the donor sheet in the form of (ET)$_{12}$(I$_3$)$_6$, whereas the remaining anion forms the anion sheet as (I$_3$)$_6$(TCE)$_4$.[83] η-(ET)I$_3$ consists of isolated ET$^+$ dimers separated by I$_3^-$ anions.[84] ϵ-, λ-, and ζ-phases are all composed of ET$^+$ dimers, but the anion parts are (I$_3^-$)(I$_8^{2-}$)$_{0.5}$ for the ϵ-phase,[85] (I$_3^-$)(I$_5^-$) for the λ-phase,[86] and (I$_2$)(I$_8^{2-}$) for the ζ-phase,[87] where I$_8^{2-}$ is a bent unit composed of I$_3^-$–I$_2$–I$_3^-$, and I$_5^-$ also has a bent structure. All these phases are reported from the Russian group, except for λ-(ET)$_2$I$_3$I$_5$, which was first reported as ζ-(ET)$_2$I$_3$I$_5$ from the Argonne group, but the Russian group reported a different ζ-phase.

In Table 2, the former six compounds (prepared by the electrochemical crystallization) exhibit metallic conductivity, while the latter four compounds (prepared from the direct reaction with iodine) contain fully oxidized ET$^+$ dimer and, consequently, are insulating. The scientists of the Argonne group have observed metallic conductivity in the ϵ- and λ-phases, which is not likely from the crystal structure, and

they have attributed the metallic conductivity to anion deficiency. The γ-phase is also an anion-incorporating phase, and the reported metallic conductivity and even superconductivity are not very likely.[82]

Yamamoto and co-workers have added diiodoacetylene (DIA) or another iodine-containing reagent as a third component in electrochemical crystallization and obtained many new charge-transfer salts (see Table 3).[88−92] The iodine-containing compounds result in Lewis acid−base interaction with anions, to construct three-component charge-transfer salts with supramolecular assemblies. The representative compound is (ET)$_2$Cl(DIA), which is a metallic β''-type salt with a quarter-filled band. When DIA is replaced by the more bulky p-bis(iodoethynyl)benzene (BIB), a metallic 3:1 salt, (ET)$_3$Cl(BIB), with a similar β''-type structure, is obtained. It is noteworthy that band filling less than quarter filling is rare in ET salts, but a 1/3+ state is realized by the use of the bulky third component. (ET)$_2$BrI$_3$(DIA) has the same structure as ϵ-(ET)$_2$I$_3$(I$_8$)$_{0.5}$, where I$_8^{2-}$ is replaced by Br$^-$ and DIA. The AuBr$_2^-$ anions in (ET)$_6$(AuBr$_2$)$_6$Br(TIE)$_3$ are incorporated in the donor sheet, similarly to the τ-phase salts (section 6.5 and Figure 21). The donors have a 7/6+ average charge, and this is the only salt based on TTF-type donors which shows metallic conductivity despite the donor charge exceeding 1+.

4.2. ET Salts with Transition Metal Anions

Non-quarter-filled ET salts with transition metal anions (including anions with Hg, Zn, and Cd atoms) are listed in Table 4. In addition to the previously described κ-(ET)$_4$Hg$_{3-\delta}$X$_8$, many other mercury halide salts of ET have been reported, and some of them are not quarter-filled. Among them, (ET)$_5$Hg$_3$Br$_{11}$ is a metal down to 120 K.[95] The Hg$_3$Br$_{11}$ unit has a 5− charge, and 3/10 of the donors are incorporated in the anion sheet in the form of ET^{2+} (E and F in Figure 7). Accordingly, the other donor molecules, which construct sevenfold β-like stacks, have a 4/7+

Table 3. Three-Component Salts with Iodine-Containing Neutral Molecules

compound[a]	charge	conductivity[b]	structure	ref
(ET)$_3$Cl(BIB)	1/3+	M (0.8 Ω cm)	β''-type	88, 89
(ET)$_3$Br(BIB)	1/3+	M (0.01 Ω cm)	β''-type	89
(ET)$_3$Br(DFTIB)	1/3+	I (3 Ω cm)	δ-type	90
(ET)$_2$Cl(DIA)	1/2+	M (0.05 Ω cm)	β''-type	88, 91
(ET)$_2$Br(DIA)	1/2+	M (0.6 Ω cm)	β''-type	88, 91
(ET)$_2$Cl(BIB)(PhCl)$_x$	1/2+			89
(ET)$_6$Br$_3$(TIE)$_3$(BIB)$_2$	1/2+	I	BIB mixed	89
(ET)$_3$Br$_2$(DFTIB)	2/3+	I (300 Ω cm)		90
(ET)$_2$Cl$_2$(DIA)(TIE)	1+	I (20 Ω cm)	mixed	88
(ET)$_2$Br$_2$(DIA)(TIE)	1+	I (700 Ω cm)	mixed	88
(ET)$_2$BrI$_3$(DIA)	1+	I	ϵ-type	89
(ET)$_2$Br$_2$(DFTIB)	1+	I (100 Ω cm)	1D chain	90
(ET)$_2$Br$_2$(DFTIB)$_3$(PhCl)$_x$	1+	I (1 Ω cm)	mixed	90
(ET)$_6$(AuBr$_2$)$_6$Br(TIE)$_3$	7/6+	M (0.1 Ω cm)	mixed, τ-like	88
(EDT-TTF)$_4$Br$_2$I$_3$(TIE)	3/4+	I (7 Ω cm)	mixed	88
(EDT-TTF)$_4$BrI$_2$(TIE)$_5$	3/4+	I (0.1 Ω cm)	mixed	88
(EDT-STF)$_4$I$_3$(TIE)$_5$	3/4+	I (0.1 Ω cm)	mixed	89
(TMTSF)Br(TIE)	1+	I (3000 Ω cm)	1D chain	89

[a] BIB = p-bis(iodoethynyl)benzene. DFTIB = 1,4-difluoro-2,3,5,6-tetraiodobenzene. DIA = diiodoacetylene. TIE = tetraiodoethylene. EDT-TTF = ethylenedithio-TTF. EDT-STF = ethylenedithiodiselenadithiafulvalene. [b] M = metals down to helium temperatures. I = insulators at room temperature and RT conductivity.

Table 4. Non-Quarter-Filled ET Salts with Transition Metal Anions

compound	charge	conductivity[b]	structure	ref
$(ET)_4Hg_{2.78}Cl_8$	~1/2+	T_{SC} = 1.8 K (12 kbar)	κ-type	26, 28
$(ET)_4Hg_{2.89}Br_8$	~1/2+	T_{SC} = 4.3 K	κ-type	26, 30
$(ET)_4Hg_3I_8$	1/2+	I (3 S cm^{-1})	α-type?	42
$(ET)Hg_{0.766}(SCN)_2$	0.468+	I		93, 94
$(ET)_5Hg_3Br_{11}$	4/7+	T_{MI} = 120 K	β	95
$(ET)_3(HgCl_3)_2$	2/3+	I (10^{-2} S cm^{-1})	δ-like	96
$(ET)_3(HgBr_3)_2$	2/3+	I	β''-type	97
$(ET)_2HgBr_4(TCE)$	1+	I		93
$(ET)HgBr_3$	1+	I (10^{-4} S cm)	dimer	95
$(ET)_4Hg_2I_{14}$			mixed	98
$(ET)_2Cd_3I_6$			θ-type?	99
$(ET)Cd_{0.66}(SCN)_2$	0.68+	I (4 S cm^{-1})	θ-type	100
$(ET)Zn(SCN)_3$	1+	I (0.006 S cm^{-1})	ladder	101
$(ET)_3(ZnCl_4)_2$	1+	I (0.4 S cm^{-1})	β'-type	102
$(ET)_3(MnCl_4)_2$	1+	I (0.04 S cm^{-1})	β'-type	103
$(ET)AuCl_2$	1/2+	I (0.01 S cm^{-1})	mixed	104
$(ET)AuCl_2AuCl_4$	1+	I (0.25 S cm^{-1})	mixed	105
$(ET)AuBr_2Cl_2$	1+	I		106
$(ET)_3AuBr_4$	2/3+	T_{MI} = 125 K	α-type	107
$(ET)Ag_{1.6}(SCN)_2$	0.4+	I (0.013 S cm^{-1})	θ-type	108
$(ET)Ag_{2.4}Br_3$	0.6+		θ-type	109
$(ET)Ag_4(CN)_5$	1+		T_{MI} = 100 K	110
$(ET)_3Ag_{6.4}I_8$	0.53+	T_{MI} = 60 K	θ-type	111
$(ET)_2K_{1.4}Co(SCN)_4$	0.3+	T_{MI} = 130 K	α''-type	97
$(ET)_3CuCl_4H_2O$	2/3+	M	β''-type	112
$(ET)_3NiCl_4H_2O$	2/3+	M	β''-type	113, 107
$(ET)_3CuBr_4$	2/3+	I (0.6 S cm^{-1})	α-type	114
$(ET)_3CuCl_2Br_2$	2/3+	I (0.7 S cm^{-1})	α-type	115
$(ET)CuCl_2$	1+		β	116
$(ET)Cu_3I_4$	1+			117
$(ET)Cu_2Br_4$	2+	I (0.016 S cm^{-1})		209
$(ET)_2Cu_6Br_{10}$	1+	I (2.1 S cm^{-1})		209
$(ET)_3Cu_4Br_6$	2/3+	T_{MI} = 270 K		209
$(ET)_2Cu_2Br_4$	1+	I (0.00054 S cm^{-1})		209
$(ET)_2Cu_3Br_7 (H_2O)$	2+	T_{MI} = 50 K		209
$(ET)_2Cu_6Br_{10} (H_2O)_2$	2+	I (0.051 S cm^{-1})		209
$(ET)FeCl_4$	1+	I	dimer	118
$(ET)FeBr_4$	1+	I (10^{-6} S cm^{-1})	dimer	119
α-$(ET)_3(ReO_4)_2$	2/3+	T_{MI} = 88 K	β''	120
β-$(ET)_3(ReO_4)_2$	2/3+	T_{MI} = 100 K		120
γ-$(ET)_3(ReO_4)_2$	2/3+	I	β''	120
$(ET)ReO_4(THF)_{0.5}$	1+	I (10^{-5} S cm^{-1})	dimer	64
$(ET)_4Re_6S_5Cl_9$	1/4+	M		121
$(ET)_4Re_6Se_5Cl_9$	1/4+	T_{MI} = 20 K		121
$(ET)Re_6Se_5Cl_9(DMF)_2$[a]	1+	I (4 × 10^{-6} S cm^{-1})		122
$(ET)_3Re_2(NCS)_{10}CH_2Cl_2$	1+	I (0.01 S cm^{-1})	mixed	123
$(ET)[MoOCl_4(H_2O)]$	1+	I (0.5 S cm^{-1})	mixed	123, 124
$(ET)_3[V(dmit)_3]_2$	2/3+	I (3 S cm^{-1})		125

[a] DMF = dimethylformamide. [b] I = insulators at room temperature and RT conductivity. M = metals down to helium temperatures.

charge on average; this value is again slightly larger than the quarter-filled value. The ground state of this compound is nonmagnetic. (ET)HgBr$_3$ is an insulator, but from the optical measurement, the on-site Coulomb repulsion of ET is estimated to be 0.69 eV, assuming the one-dimensional chain model.[126]

(ET)$_3$(MnCl$_4$)$_2$ and (ET)$_3$(ZnCl$_4$)$_2$ are isostructural salts (Figure 8),[102,103] in which one of the three ET molecules, B, is again incorporated in the anion sheet in the form of ET^{2+} and the other two ET$^+$ molecules, A and A′, construct a β'-type sheet. Because the β'-phase is a strongly dimerized structure, these salts are electrical insulators. Recently, chemical doping to this structure has been achieved, and metallic states down to low temperatures were realized (section 6.3).

Also (ET)Zn(SCN)$_3$ has ET$^+$, but two β''-like chains of ET are isolated by the surrounding anions, though

the "chain direction" is the transverse (30°) direction of the ET molecules.[101] As a result, a double chain structure of ET molecules is realized. The magnetic susceptibility of this compound drops to a spin singlet state at low temperatures, so that this compound is regarded as a spin ladder of ET molecules (with a spin gap of 340 K). Another spin ladder system is recently found in (ET)[Co(mnt)$_2$] (mnt = maleonitrile thiocyanate).[127]

In (ET)AuCl$_2$, half of the AuCl$_2$ anion is incorporated in the donor sheet, but the donor charge estimated from the bond lengths is 1/2+, so that the incorporated AuCl$_2$ unit is neutral.[104] The resulting formal charge of gold is 2+; this is quite an unusual charge for gold. The same happens in (ET)-AuCl$_2$AuCl$_4$, where AuCl$_4^-$ constructs the anion layer and the AuCl$_2$ unit is again sandwiched by the ET$^+$ donor molecules, resulting in 2+ gold.[105] These
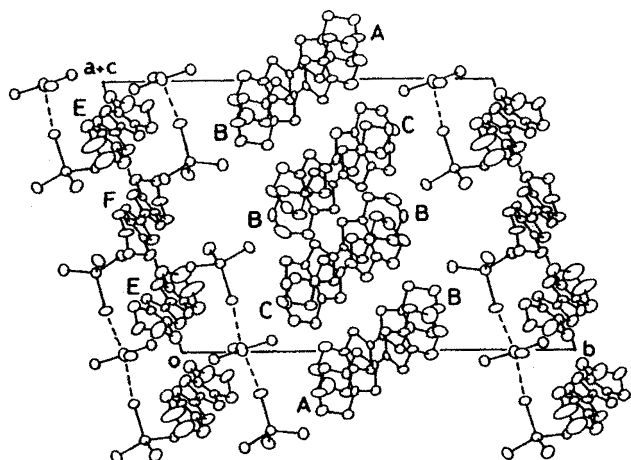
Figure 7. Crystal structure of $(ET)_5Hg_3Br_{11}$. Reprinted with permission from ref 95. Copyright 1987 The Chemical Society of Japan.
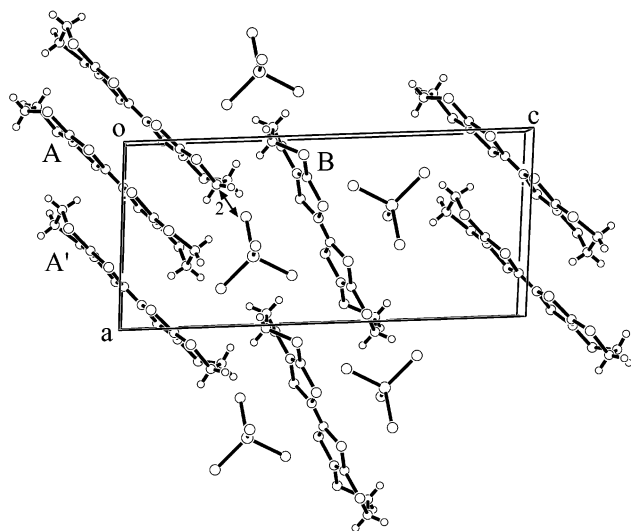
Figure 8. Crystal structure of $(ET)_3(MnCl_4)_2$.

mysteries demonstrate that inorganic anions sandwiched by organic donors tend to exhibit anomalous formal charge, or in that case we should be careful to estimate the donor charge from the bond lengths.

There are many "nonstoichiometric" transition metal halides and thiocyanates; examples are $(ET)Ag_{2.4}Br_3$, $(ET)_3Ag_{6.4}I_8$, $(ET)Ag_{1.6}(SCN)_2$, $(ET)Cd_{0.66}$-$(SCN)_2$, and $(ET)_2K_{1.4}Co(SCN)_4$. These compounds are constructed of polymeric anions, and the deficiency of the metal atom is intrinsic. These compounds usually show relatively high electrical conductivity.

$(ET)_3CuCl_4H_2O$ is known as the first metallic conductor with a paramagnetic anion.[112] The anion is a strongly flattened tetrahedron, and the copper is 2+. Accordingly, the donor charge is 2/3+, which forms a β''-type arrangement. The structure of this compound is analogous to those of $(ET)_3(ClO_4)_2$ and $(ET)_3Cl_2(H_2O)_2$.[112] $(ET)_3NiCl_4H_2O$ is prepared by an independent research group,[107,113] and this Ni compound is isostructural to the Cu compound. These compounds show a metallic conductivity down to low temperatures.

$(ET)_3CuBr_4$ also has 2+ copper in $CuBr_4{}^{2-}$.[114] Owing to the charge separation like $A^+A^+B^0$ (Figure
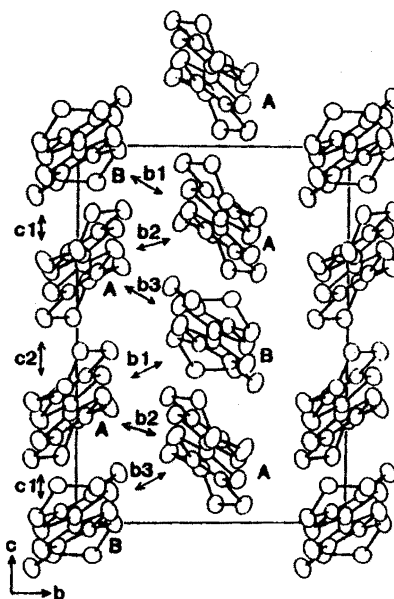
Figure 9. Crystal structure of $(ET)_3CuBr_4$, where the donor charge is $A^+A^+B^0$. Reprinted with permission from ref 105. Copyright 1986 The Chemical Society of Japan.

9), this compound is a semiconductor even at room temperature. Nonetheless, this compound shows intriguing magnetic phenomena,[128] where the donor spin disappears accompanied by the structural phase transition at 59 K, and the Cu spin becomes antiferromagnetic at $T_N = 7.65$ K.

Recently, several ET salts in high oxidation states, $(ET)Cu_2Br_4$ (2+), $(ET)_2Cu_6Br_{10}$ (1+), $(ET)_3Cu_4Br_6$ (2/3+), $(ET)_2Cu_2Br_4$ (1+), $(ET)_2Cu_3Br_7$ (H_2O) (2+), and $(ET)_2Cu_6Br_{10}$ $(H_2O)_2$ (2+) have been obtained by the direct reaction of ET and $CuBr_2$.[209] Although these compounds are relatively poor conductors, the sulfur atoms directly coordinate to copper atoms, and the ET molecules and the anions form characteristic alternating arrangements.

There are several salts containing metal clusters such as $Re_6Se_5Cl_9{}^-$. Since $Re_6Se_5Cl_9{}^-$ is a monoanion, the donors in $(ET)_4Re_6Se_5Cl_9$ and $(ET)_4Re_6S_5Cl_9$ have a 1/4+ charge, and the salts are metals.[121] $(ET)Re_6Se_5Cl_9(DMF)_2$ has ET^+ and is an insulator.[122] There are a considerable number of polymetalate salts. For example, $(ET)_8[SiW_{12}O_{40}]$ is quarter-filled, but by changing Si to other elements, such as P, H_2, Co, Cu, and Fe, the donor charge changes from 1/2+ (for Si^{4+}) to 3/4+ (for Cu^{2+}). More polymetalate salts have been reviewed by Coronado and Gomez-Garcia.[129]

4.3. BO Salts

Several non-quarter-filled BO salts are listed in Table 5 (BO = bis(ethylenedioxy)tetrathiafulvalene). In $(BO)_{2.4}I_3$, which is metallic down to low temperatures, the donors and the anions construct incommensurate sublattices.[94,130] Similarly to the ET iodides, $(BO)I_3$ and $(BO)(I_3)_2$ are obtained by the direct reaction of BO with iodine in acetonitrile, and in these salts some of the $I_3{}^-$ ions are incorporated in the donor sheet.[131] In the superconductor, $(BO)_3Cu_2(NCS)_3$, the donor sublattice and the anion

**Table 5. Non-Quarter-Filled BO Salts**

compound	charge	conductivity[a]	structure	ref
$(BO)_{2.4}I_3$	0.417+	M	β''	130
$(BO)I_3$	1+	I (10^{-6} S cm)	mixed	131
$(BO)(I_3)_2$	2+	I ($<10^{-9}$ S cm)	mixed	131
$(BO)_3Cu_2(NCS)_3$	1/3+	$T_{SC} = 1$ K	β''	132
$(BO)_5Hg_{1.9}Br_{6.8}$	0.60+	M	β''	133
$(BO)_9(HgBr_4)_2(DCE)_5$	0.444+	M	β''	133
$(BO)_5[CsHg(SCN)_4]_2$	0.4+	M	β''	134

[a] I = insulators at room temperature and RT conductivity. M = metals down to helium temperatures.

sublattice are reported to be independent.[132] The donor structure is the β''-type, as is the case for many other BO compounds, and the anion sublattice, composed of infinite chains of $Cu_2(NCS)_3$, is three times larger than the donor sublattice.


BO
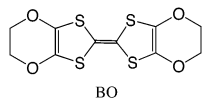
The chlorine-containing salt which has θ-type structure and shows a metallic behavior has first been reported to be 1:1 as $(BO)Cl(H_2O)_x$,[135] but the observations of the Shubnikov−de Haas and angle-dependent magnetoresistance oscillations indicate quarter filling.[136] Consequently, the correct formula should be θ-$(BO)_2Cl(H_2O)_3$.[137]

The Fermi surface of $(BO)_5[CsHg(SCN)_4]_2$ has also been verified from the observation of the Shubnikov−de Haas oscillations.[134] Band fillings of several BO complexes, such as $(BO)_{2.4}I_3$, $(BO)_9(HgBr_4)_2(DCE)_5$, and $(BO)_5[CsHg(SCN)_4]_2$, are around 0.4 and are a little smaller than the quarter filling. In addition, there are several BO complexes with organic polycyanide anions whose donor charge is 0.4.[138] This makes a sharp contrast to the case of ET, in which the most preferable band filling tends to slightly exceed quarter filling (0.5−0.67). BO is, however, a stronger donor than ET.[139]

4.4. Other TTF Donors

For MT (bis(methylenedithio)tetrathiafulvalene), the 2:1 composition is most common, but several 3:1 salts such as $(MT)_3PF_6(TCE)$ and $(MT)_3ClO_4(TCE)$ are reported.[140]
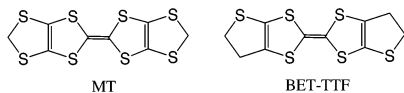
MT   BET-TTF

BET-TTF (bis(ethylenethio)tetrathiafulvalene) gives several non-quarter-filled salts such as $(BET-TTF)_3$-$(ReO_4)_2$ and $(BET-TTF)_9(ReO_4)_4(THF)_2$.[141,142] $(BET$-$TTF)_3(ReO_4)_2$ has a similar structure to $(ET)_3(MnCl_4)_2$ (Figure 8), where 1/3 of the donors is incorporated in the anion sheet (molecule B), and the rest of the donors form a β'-structure (molecule A). The anion is, however, monovalent, instead of the divalent $MnCl_4^{2-}$, so that the charge is $A^{1/2+}A^{1/2+}B^+$ instead of $A^+A^+B^{2+}$ in the $MnCl_4$ salt. Accordingly, this salt

is metallic down to 125 K.[141] $(BET-TTF)_9(ReO_4)_4(THF)_2$ has a β-like structure and is metallic down to 75 K.

4.5. $(DTEDT)_3Au(CN)_2$

Non-quarter-filled superconductors are summarized in Table 6. $(ET)_4Hg_{2.78}Cl_8$, $(ET)_4Hg_{2.89}Br_8$, $(ET)_3$-

Table 6. Non-Quarter-Filled Superconductors

compound	charge	T_{SC}	structure	ref
$(ET)_4Hg_{2.78}Cl_8$	~1/2+	1.8 K (12 kbar)	κ-type	24, 26
$(ET)_4Hg_{2.89}Br_8$	~1/2+	4.3 K	κ-type	24, 27
$(ET)_3Cl_2(H_2O)_2$	2/3+[a]	2K (16 kbar)	β''	59, 60, 71, 72
$(BO)_3Cu_2(NCS)_3$	1/3+	1 K	β''	132
$(DTEDT)_3Au(CN)_2$	1/3+	4 K	uniform	143
$(MDT-TSF)X_x{}^b$	~0.423+	4.0−5.5 K	uniform	9, 10
$(MDT-ST)X_x{}^c$	~0.423+	3.2−3.6 K	uniform	144

[a] $T_{MI} = 100$ K, nonmagnetic. [b] $X_x = (AuI_2)_{0.436}$, $I_{1.27}$, $I_{1.19}Br_{0.08}$, $I_{0.77}Br_{0.52}$, and $I_{1.27-\delta}Cl_\delta$ ($\delta \sim 0$). [c] $X_x = I_{1.27}$, $I_{1.27-\delta}Br_\delta$ ($\delta \sim 0.2$), and $I_{1.27-\delta}Cl_\delta$ ($\delta \sim 0$).

$Cl_2(H_2O)_2$, and $(BO)_3Cu_2(NCS)_3$ are discussed previously. $(DTEDT)_3Au(CN)_2$ is the first and still the only superconductor containing the vinylog moiety (DTEDT = 2-(1,3-dithiol-2-ylidene)-5-(2-ethanediylidene-1,3-dithiole)-1,3,4,6-tetrathiapentalene).[143,145] In
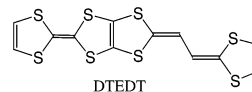
DTEDT

the crystal, the vinylog group is arranged on the same side, namely in a head-to-head manner (Figure 10).
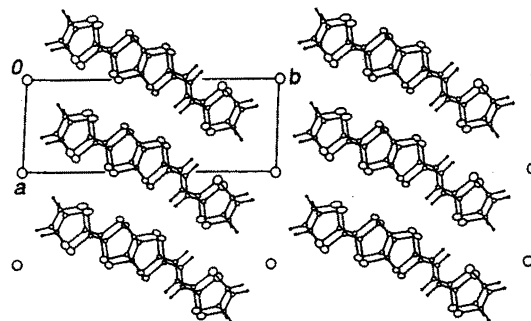
Figure 10. Crystal structure of $(DTEDT)_3Au(CN)_2$. Reprinted with permission from ref 143. Copyright 1995 Wiley Interscience.

Since the donor molecule does not have an inversion center and the donor cell involves only one molecule, the space group is non-centrosymmetric ($P1$). If we neglect the threefold periodicity coming from the anion lattice, the donors have a perfectly uniform stack.[146] The uniform stack, however, has considerable interstack interactions, and the calculated Fermi surface is closed. The complexes of other anions, such as $(DTEDT)_3SbF_6$ and $(DTEDT)_3Ag(CN)_2$, have the same structure, and the resistivity slightly increases at low temperatures, but superconductivity is not observed.[147] The selenium-substituted donors have been prepared, and the complexes have the same structure as well, but superconductivity is not found.[148]

5. Half-Filled Metallic Salts

As described in section 2, half-filled compounds are inherent Mott insulators (Figure 1a). Up to now,

however, two series of half-filled compounds have been reported to be metals at room temperature: (TTM-TTP)I$_3$ and (DMTSA)BF$_4$.[5,6] Interestingly, both compounds were reported in the same issue of the same journal.

5.1. (TTM-TTP)I$_3$ and Similar Salts

The so-called BDT-TTP (2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene) or simply TTP donor consists of two fused TTF molecules.[149] Since this molecule has four 1,3-dithiole rings, this donor is oxidized up to a tetracation (4+). The tetramethylthio-substituted derivative (TTM-TTP) gives a number of salts.

BDT-TTP

Three kinds of iodide salts are known for this donor: (TTM-TTP)$_2$I$_3$, (TTM-TTP)I$_3$, and (TTM-TTP)-(I$_3$)$_{5/3}$.[5] All salts are obtained fr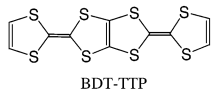om electrochemical crystallization, but the former two are also prepared by the interdiffusion method. The donors in (TTM-TTP)$_2$I$_3$ formally have a 1/2+ charge, while one-quarter of the donors are incorporated in the anion sheet. The remaining three-quarters construct trimerized columns, and this compound is an electrical insulator with a small room-temperature conductivity ($\sigma_{RT} = 0.03$ S cm^{-1}). This is a minority phase in the electrochemical crystallization.

(TTM-TTP)I$_3$ is the majority phase of the electrocrystallization. A unit cell ($P\bar{1}$) contains only one molecule located on an inversion center, and the donors are uniformly stacked (Figure 11). Since the
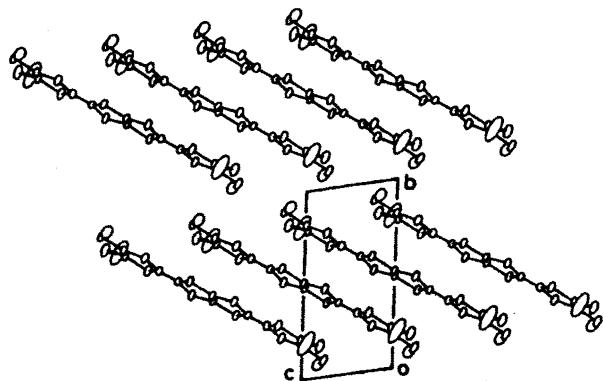
Figure 11. Uniform stack in (TTM-TTP)I$_3$. Reprinted with permission from ref 5. Copyright 1994 The Chemical Society of Japan.

TTP molecule is a long molecule, in the stack the molecules slip as much as 4.8 Å along the molecular long axis. Accordingly, the donors are more than 45° tilted from the stacking direction, and one TTF part overlaps with another side of the TTF of the adjacent TTP molecule.

The discrete I$_3$$^-$ unit is also located on an inversion center, and the composition is exactly 1:1. Since the donors construct one-dimensional columns, and the sides of the donors are blocked by the methylthio parts, the transverse interaction is less than 1/20 of the intrastack interaction, and the energy band is

highly one-dimensional. The donor charge is 1+, and the one-dimensional band is half-filled.

The conductivity is as high as 700 S cm^{-1} at room temperature and is almost constant down to 160 K, below which the resistivity increases (Figure 12a).
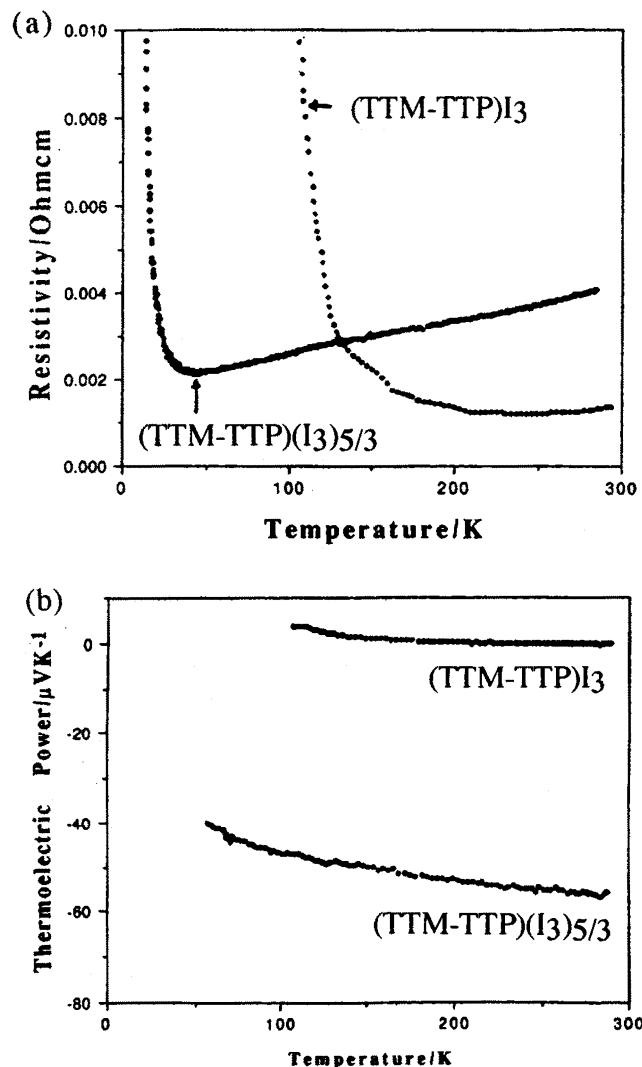
Figure 12. (a) Electrical resistivity and (b) thermoelectric power of (TTM-TTP)I$_3$ and (TTM-TTP)(I$_3$)$_{5/3}$. Reprinted with permission from ref 5. Copyright 1994 The Chemical Society of Japan.

However, the magnitude of the resistivity increase is somewhat dependent on the sample, and a clear increase occurs below 120 K. The thermoelectric power is exactly zero in the metallic temperature region, verifying the half-filled nature of the energy band (Figure 12b). The MI transition temperature lowers under pressure, but the shift is very gradual; under 11.5 kbar the MI transition still takes place at 100 K and is not completely suppressed.[150] From the optical reflectance spectrum, the on-site Coulomb repulsion U of (TTM-TTP)I$_3$ is evaluated to be 0.49 eV, assuming an infinite Hubbard chain;[151] this value is about two-thirds that of the ET molecule (0.69 eV), obtained assuming the same model.[126]

The static magnetic susceptibility was first reported to be constant even in the insulating region.[150] If this is true, the low-temperature phase is a

paramagnetic Mott insulator as depicted in Figure 1a. The drop of the susceptibility was later observed below 120 K (Figure 13a).[152] The Pauli susceptibility
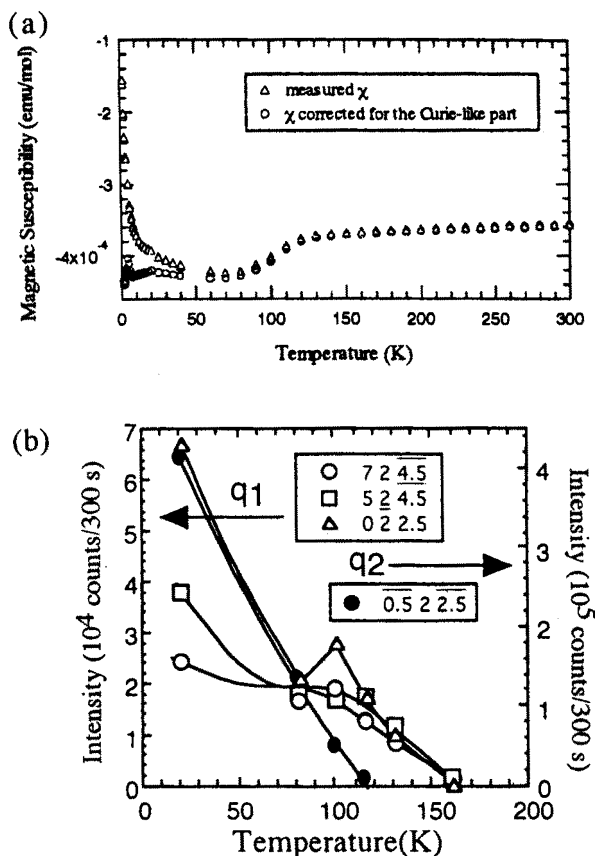
Figure 13. (a) Static magnetic susceptibility of (TTM-TTP)I$_3$.[152] (b) Temperature dependence of q_1 and q_2 satellite reflections in (TTM-TTP)I$_3$.[153] Reprinted with permission from refs 152 and 153. Copyright 1999 Elsevier.

estimated from the half-filled one-dimensional band and the calculated bandwidth, 0.64 eV, is as small as 0.64×10^{-4} emu/mol (compared with the value of the typical ET compounds, 4×10^{-4} emu/mol), because half filling corresponds to the minimum of

the density of states in a one-dimensional band. The observed drop of the susceptibility corresponds to this small value, and the precise observation is comparatively difficult. The drop of spin susceptibility has also been observed in the ESR measurement.[153] The low-temperature X-ray measurements have revealed two kinds of $2k_F$ scatterings: $q_1 = (0, 0, 1/2)$ grows from 160 K, and $q_2 = (1/2, 0, 1/2)$ develops below 110 K (Figure 13b). The exponential decay of T_1^{-1} in ^{13}C NMR also proves the nonmagnetic ground state.[154] Then the ground state is more appropriately represented by Figure 1b rather than Figure 1a. In the insulating state, however, splittings of NMR spectra and Raman spectra have been observed,[155,156] indicating some kind of charge disproportionation. Detailed analysis of the Raman spectra and X-ray results demonstrates the loss of inversion symmetry on the donor molecule owing to the q_1 modulation. Accordingly, each TTM-TTP molecule has the same 1+ charge, but the left and the right TTF parts of one TTM-TTP molecule have different charges.[156]

In addition to (TTM-TTP)I$_3$, several other 1:1 complexes have been prepared based on TTM-TTP, as listed in Table 7. (TTM-TTP)AuI$_2$ and (TTM-TTP)-AuBr$_2$ form dimerized β-type columns, while the conductivities are relatively high, 10–40 S cm^{-1}.[162] (TTM-TTP)[C(CN)$_3$], (TTM-TTP)FeBr$_{1.8}$Cl$_{2.2}$, and (TTM-TTP)Fe$_{0.9}$Ga$_{0.1}$Cl$_4$ are also metallic compounds with uniform columns.[158–160] These compounds are isostructural compounds with a space group, $C2/c$, different from the $P\bar{1}$ of (TTM-TTP)I$_3$, but the structure of the highly one-dimensional column is the same (Figure 14). In particular, the MI transition temperature of (TTM-TTP)[C(CN)$_3$], 70 K, is considerably lower than that of (TTM-TTP)I$_3$.[157,158] This compound shows a drop of spin susceptibility in the insulating region.[158] If we use pure anions such as FeX$_4$ and GaX$_4$ (X = Cl and Br), we obtain strongly dimerized β'-phases such as (TTM-TTP)-FeCl$_4$(PhCl)$_{0.5}$,[164,165] which are highly resistive insulators (0.05–0.2 S cm^{-1}), while if we use anions with mixtures of Fe and Ga, or Cl and Br, we obtain the uniform phases.[159,160] In the same way, we can alloy

Table 7. Half-Filled TTM-TTP Complexes and the Analogues

compound	charge	structure^a (c1/c2)	σ_{RT} (S cm^{-1})	T_{MI} or E_a	ref
(TTM-TTP)I$_3$	1+	U (1.0)	700	160 K	5
(TTM-TTP)[C(CN)$_3$]	1+	U (1.0)	500	70 K	157, 158
(TTM-TTP)FeCl$_{1.8}$Br$_{2.2}$	1+	U (1.0)	1000	160 K	159
(TTM-TTP)Fe$_{0.9}$Ga$_{0.1}$Cl$_4$	1+	U (1.0)	190	160 K	160
(TTM-TTP)Fe$_{0.95}$Co$_{0.05}$Cl$_4$	1.025+	U (1.0)	350	200 K	8
(TTM-TTP)Ga$_{0.7}$Co$_{0.3}$Cl$_4$	1.3+	U (1.0)	140	0.02 eV	8
(TTM-TTP)Fe$_{0.6}$Co$_{0.4}$Cl$_4$	1.4+	U (1.0)	85	0.025 eV	8
(TTM-TTP)Mn$_{0.1}$Co$_{0.9}$Cl$_4$	2+	U (1.0)	0.7	0.11 eV	8
(TTM-DSDTP)GaCl$_4$	1+	U (1.0)	280	60 K	161
(TTM-TTP)AuI$_2$	1+	Dβ (0.70)	10	0.04 eV	162
(TTM-TTP)AuBr$_2$	1+	Dβ (0.90)	40	0.06 eV	162
(TTM-TTP)HgI$_3$(TCE)	1+	Dβ (0.68)	5	0.04 eV	163
(TTM-TTP)FeCl$_4$(PhCl)$_{0.5}$	1+	Dβ' (0.08)	0.01	0.06 eV	164
(TTM-TTP)FeBr$_4$(PhCl)$_{0.5}$	1+	Dβ' (0.26)	0.18	0.06 eV	164
(TTM-TTP)GaCl$_4$(PhCl)$_{0.5}$	1+	Dβ' (0.26)	0.01	0.09 eV	160
(TTM-TTP)GaBr$_4$(PhCl)$_{0.5}$	1+	Dβ' (0.22)	0.07	0.05 eV	160
(TTM-TTP)GaCl$_2$Br$_2$(PhCl)$_{0.5}$	1+	Dβ' (0.20)	0.03	0.07 eV	160
(TTM-DSDTP)I$_3$	1+	trimer	2.3	0.11 eV	161

^{a} U = uniform. D = dimerized. c1/c2 is the ratio of intrachain transfers, as a measure of the degree of dimerization. c1/c2 = 1.0 represents a uniform column.
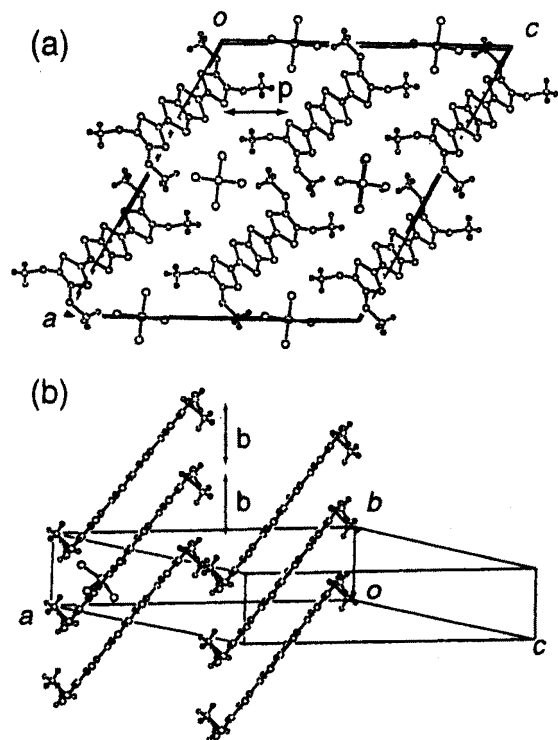
Figure 14. Crystal structure of (TTM-TTP)FeCl$_{1.8}$Br$_{2.2}$: (a) view along the stacking axis; (b) uniform structure of the columns around $x = 0.25$. The columns around $x = 0.75$ have opposite inclination.[159]

divalent metals such as Co^{2+} and Mn^{2+} to the uniform phase, achieving the band filling control;[8] this is described in section 6. Selenium substitution to the TTM-TTP molecule has been achieved.[161] Among them, (TTM-DSDTP)GaCl$_4$, which is isostructural to (TTM-TTP)FeBr$_{1.8}$Cl$_{2.2}$, maintains the metallic conductivity down to 60 K (TTM-DSDTP = 2,5-bis(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)-1,3,4,6-diselenadithiapentalene).

TTM-DSDTP
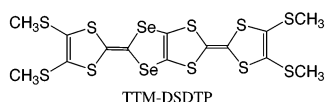
Finally, in the third phase (TTM-TTP)(I$_3$)$_{5/3}$, the formula shows that the donor has a 5/3+ charge. This is nearly a 2+ charge, but this complex exhibits metallic conductivity. This phase is frequently obtained, but in the case of TTM-TTP it is not obtained as a single phase. This phase is, however, easily distinguished under a microscope by the characteristic copper luster. Owing to the high symmetry, the crystal structure was not solved in the earlier stage,[5] whereas the crystal structure was finally solved by assuming donor disorder under an orthorhombic lattice (see Figure 15).[166] The donors construct one-dimensional columns similar to those of (TTM-TTP)-I$_3$. There is one discrete I$_3^-$ anion that is perpendicular to the donor stacks, and one infinite iodine chain parallel to the donor stacks. The average I−I spacing of the linear chain corresponds to half of the donor unit cell, so that the composition is $1 + ^2/_3 = ^5/_3$. The linear anion shows a superlattice corresponding to one and a half donor cells, in which I$_3^-$ is the

Figure 15. Crystal structure of (TTM-TTP)(I$_3$)$_{5/3}$. Reprinted with permission from ref 166. Copyright 1997 The Chemical Society of Japan.

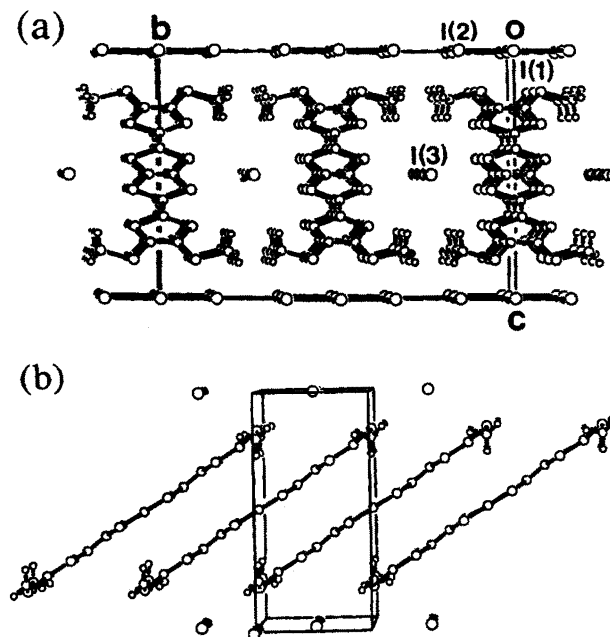repeating unit. The Raman spectrum also proves that the infinite chain consists of I$_3^-$; then the donor charge is 5/3+.[167]

The conductivity is 200 S cm^{-1} at room temperature, and the temperature dependence is metallic down to 20 K, below which the resistivity increases (see Figure 12a).[5] The increase somewhat depends on the samples,[168] and the low-temperature phase is paramagnetic,[169] so that the insulating state is attributed to weak localization coming from the disorder. The increase of the resistance is almost suppressed under pressure.[168,169] Since the 5/3+ donor charge corresponds to the 1/6-filled HOMO band, the thermoelectric power is negative (-58 μV/K), indicating electron transport (Figure 12b).[5] The selenium analogues, TSM-TTP (2,5-bis(4,5-bis(methylseleno)-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene),[170] DTM-DSM-TS-TTP (2-(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)-5-(4,5-bis(methylseleno)-1,3-diselenol-2-ylidene)-1,3,4,6-tetrathiapentalene),[161] and TSM-BDS-TTP (2,5-bis(4,5-bis(methylseleno)-1,3-diselenol-2-ylidene)-1,3,4,6-tetrathiapentalene), form the isostructural salts. In particular, (TSM-BDS-TTP)-(I$_3$)$_{5/3}$ exhibits metallic conductivity down to low temperatures, even at ambient pressure. Although the columnar structure of (TTM-TTP)(I$_3$)$_{5/3}$ is similar to that of (TTM-TTP)I$_3$, (TTM-TTP)(I$_3$)$_{5/3}$ has a relatively large transverse interaction ($t_\perp/t_\parallel \sim 0.2$) through the terminal methylthio groups. The transverse interaction of the selenium compound is further enhanced ($t_\perp/t_\parallel \sim 0.7$), and the band structure is considerably two-dimensional to stabilize the metallic conductivity.

DTM-DSM-TS-TTP   TSM-BDS-TTP
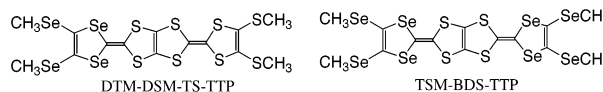
5.2. (DMTSA)BF$_4$

The donor DMTSA is designed as an analogue of tetrathiatetracene (TTT) and tetraselenatetracene (TST).[171] (DMTSA)BF$_4$ with a one-dimensional stacking structure (Figure 16) shows high room-temper-
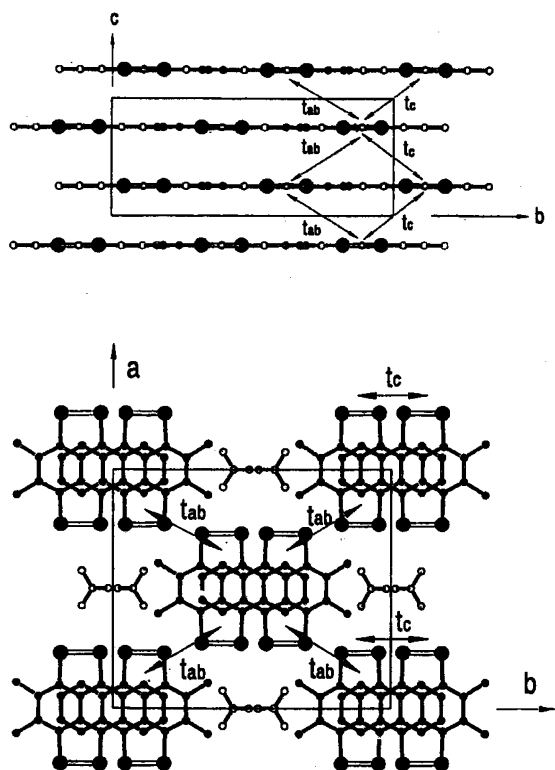
Figure 16. Crystal structure of (DMTSA)BF$_4$. Reprinted with permission from ref 174. Copyright 1998 The Physical Society of Japan.

ature conductivity, 450 S cm^{-1}, and metallic behavior.[6] The resistance exhibits a clear increase below 160 K; this is about the same temperature as that for (TTM-TTP)I$_3$. Also (DMTSA)NO$_3$ shows weakly metallic conductivity down to 200 K. The MI transition of (DMTSA)BF$_4$ is entirely suppressed above the pressure 7 kbar (Figure 17a).[172,173]

In (DMTSA)BF$_4$, the donors make zigzag columns (Figure 16), but on account of the glide symmetry, all intracolumnar transfer integrals are the same, and the column is regarded as uniform, though the Fermi level of the band structure formally comes to the zone boundary.[174] The transverse interaction is small ($t_\perp/t_\parallel \sim 1/20$), and the band structure is highly one-dimensional. From the optical reflectance spectrum, the on-site Coulomb repulsion U is evaluated to be 0.68 eV.[164] This compound also shows an almost zero thermoelectric power, reflecting the half filling.[164]

The static magnetic susceptibility has been first reported to be flat even in the insulating region,[172] but later a drop has been observed.[174] A clear drop of the spin susceptibility is also reported (Figure 17b). Because the loss of the glide symmetry is concluded from the optical and X-ray measurements,[174,175] the ground state is again considered to be the Peierls state as shown in Figure 1b. The salt of the sulfur
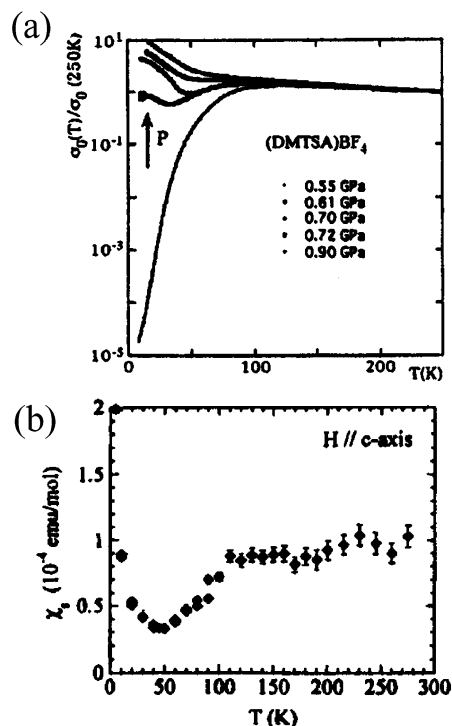
Figure 17. (a) Electrical conductivity of (DMTSA)BF$_4$ under pressure. (b) Spin susceptibility of (DMTSA)BF$_4$. Reprinted with permission from ref 174. Copyright 1998 The Physical Society of Japan.

analogue, (DMTTA)BF$_4$ is semiconductive from room temperature,[173] but a drop of the spin susceptibility is observed at 100 K (DMTTA = 2,3-dimethyltetrathioanthracene).[176] Then the high-temperature state is regarded as a Mott insulating state, and the 100 K transition is the spin Peierls transition. The measurements of X-ray photoelectron spectroscopy and the dielectric constant are reported for (DMTSA)-BF$_4$.[177]

DMTTA
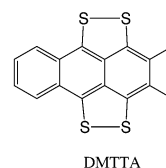
Recently, another class of 1:1 compounds such as (BETS)GaBr$_4$ has been reported to be a metal down to 20 K (BETS = bis(ethylenedithio)tetraselenafulvalene).[178]

6. Conductors with Nonstoichiometric Band Fillings

6.1. (TTF)X$_x$

Although the degree of charge transfer in such donor−acceptor complexes as (TTF)(TCNQ) is not determined from the composition, the charge-transfer degree of radical-cation salts such as (TTF)X$_x$ (X = Cl, Br, I, SCN, and SeCN, and $x \sim 0.7$) is directly determined from the composition. (TTF)X$_x$ is a classical example of "nonstoichiometric" radical-cation salts. The x value somewhat depends on the nature

of the halogen (0.77–0.80 for Cl, 0.71–0.76 for Br, and 0.70–0.72 for I) and is reported to be variable in a small range.[15] The 1:1 and 1:2 compounds, $(TTF)Cl$ and $(TTF)Cl_2$, are insulators, while $(TTF)X_x$ shows a metallic conductivity at room temperature, and an MI transition takes place around 200 K. TTF forms uniform stacks, and the anions are incorporated in the tunnels between the TTF columns. The anions have an incommensurate periodicity with the donor lattice. Since the TTF molecules of the adjacent columns are perpendicular to each other, the interchain interaction is very weak, and the electronic structure is highly one-dimensional. Below the MI transition around 200 K, the magnetic susceptibility drops to zero, and the TTF columns are modulated by the incommensurate potentials. Therefore, $(TTF)X_x$ is regarded as a typical Peierls insulator.

6.2. $(TTM\text{-}TTF)I_{2.47}$

$(TTM\text{-}TTF)I_{2.47}$ is another classical example of a well-studied nonstoichiometric radical-cation salt (TTM-TTF = tetrakis(methylthio)-TTF).[179] The X-ray

oscillation photograph of Figure 18 shows unevenly spaced layer lines which are composed of the donor

Figure 18. X-ray oscillation photograph of (TTM-TTF)-$I_{2.47}$ along the stacking axis ($b = 3.978$ Å). Reprinted with permission from ref 179. Copyright 1986 The Chemical Society of Japan.

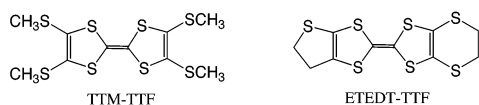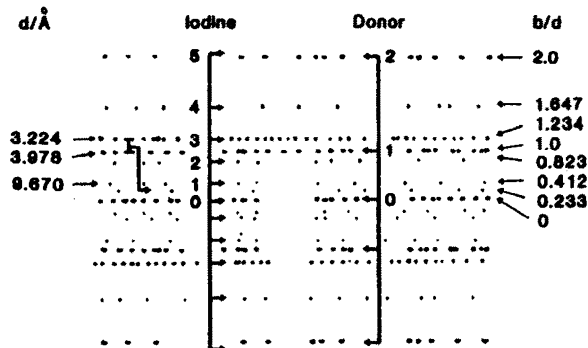sublattice and the incommensurate anion sublattice (Figure 18). The donor sublattice $b = 3.978$ Å corresponds to the spacing of the uniform donor columns, and the anion sublattice $b' = 9.670$ Å indicates the existence of I_3^-. From this ratio, the composition is determined to be $6b/b' = 2.47$, namely (TTM-TTF)-$I_{2.47}$ or $(TTM\text{-}TTF)(I_3)_{0.823}$. The existence of I_3^- is also verified from the Raman investigation.[180] The conductivity is metallic ($\sigma_{RT} = 100$–140 S cm^{-1}) down to $T_{MI} = 100$ K, below which the resistivity increases accompanied by the drop of the magnetic susceptibility.[179,181] Then the ground state is recognized as the Peierls insulator.

$(ETEDT\text{-}TTF)(I_3)_{0.42}$ has a similar incommensurate lattice, though the donor arrangement is θ-type (ETEDT-TTF = (ethylenethio)(ethylenedithio)tet-

rathiafulvalene).[182] This salt shows a semiconducting behavior ($\sigma_{RT} = 24$ S cm^{-1}), and the spin susceptibility increases with decreasing temperature.

6.3. ET and TTP Salts with Alloyed Anions

Usually two-dimensional radical-cation salts such as ET complexes are rigorously stoichiometric compounds, and even if we mix two anions having different charges in the electrocrystallization, we obtain separated compounds involving a single anion. It is therefore relatively recently that the alloyed compounds $(ET)_y(ZnCl_4{}^{2-})_{1-x}(GaCl_4{}^-)_x$ and $(ET)_y(MnCl_4{}^{2-})_{1-x}(FeCl_4{}^-)_x$ have been reported.[183] When $x = 0$, these compounds are insulators, but the 0.5% $FeCl_4^-$-doped sample shows metallic conductivity down to helium temperatures. However, higher doping (up to 4%) again leads to semiconducting samples. The crystal structures of these compounds are not reported.

A rich variety of compounds have been reported in the alloyed system of $GaCl_4^-$ and $CoCl_4{}^{2-}$.[7] When ET is electrochemically oxidized in the presence of these two anions, four different crystals are obtained, as listed in Table 8. In general, $CoCl_4{}^{2-}$ is more easily

Table 8. Polymorphism of $(ET)_n(GaCl_4{}^-)_{1-x}(CoCl_4{}^{2-})_x$

structure	n	x	charge	resistivity before and after doping[a]
λ-type	2	0.00–0.06	0.50 to 0.53+	I (3 Ω cm) → I (0.1 Ω cm)
δ'-type	2	0.00–0.14	0.50 to 0.57+	I (10 Ω cm) → I (0.3 Ω cm)
α-type	3	0.38–1.00	2/3+ to ~0.46+	$T_{MI} = 160$ K → I (0.07–0.3 Ω cm)
β'-type	3/2	0.56–1.00	1+ to ~0.67+	I (0.04 Ω cm) → $T_{MI} = 50$ K

^{a} I = insulators at room temperature.

incorporated in the crystals; for example, the nominal composition $GaCl_4^-/CoCl_4{}^{2-} = 99:1$ gives rise to nearly 50% $CoCl_4{}^{2-}$ content in α-$(ET)_3(GaCl_4{}^-)_{0.57}$-$(CoCl_4{}^{2-})_{0.43}$(TCE). The first two compounds, λ- and δ'-phases, can be considered as chemical doping variants of the pure compounds, λ-$(ET)_2GaCl_4$ and δ'-$(ET)_2GaCl_4$. By this 6–14% doping, the highly resistive semiconductors λ-$(ET)_2GaCl_4$ and δ'-$(ET)_2$-$GaCl_4$ (3 and 10 Ω cm, respectively) are transformed to the relatively conductive semiconductors λ-$(ET)_2(GaCl_4)_{0.94}(CoCl_4)_{0.06}$ and δ'-$(ET)_2(GaCl_4)_{0.86}$-$(ZnCl_4)_{0.14}$ (0.1 and 0.3 Ω cm).

The parent compound of the third phase, α-$(ET)_3$-$(GaCl_4{}^-)_{1-x}(CoCl_4{}^{2-})_x$(TCE) ($x = 0.38$–0.46), is α-$(ET)_3CoCl_4$(TCE), which is basically isostructural to α-$(ET)_3CuBr_4$ (Figure 9). Similarly to the $CuBr_4$ compound, all these compounds show charge order. The parent pure $CoCl_4{}^{2-}$ compound is metallic down to 160 K, but the alloyed compounds ($x = 0.38$–0.46) are semiconductors.

The parent compound of the fourth phase is β'-$(ET)_3(MnCl_4)_2$ (Figure 8), where 1/3 of the donors are incorporated in the anion sheet in the form of ET^{2+} (molecule B) and the rest of the ET^+ donors form a β'-structure (molecule A). The doped electron

mainly enters in the β'-sheet, so that the charges in β'-$(ET)_3(GaCl_4^-)_{0.66}(CoCl_4^{2-})_{1.34}$ are approximately $A^{0.67+}A^{0.67+}B^{2+}$. Although the parent phase is a semiconductor, this doped compound is a metal down to 50 K and maintains metallic conductivity down to low temperatures under the pressure 12.6 kbar (Figure 19). When it is doped with $FeCl_4^-$, instead of $GaCl_4^-$,
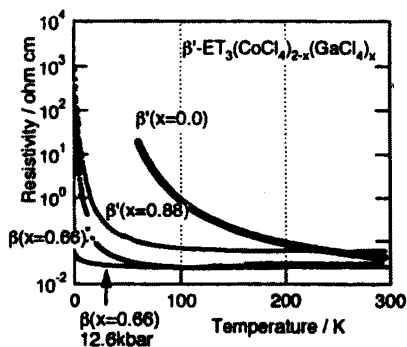
Figure 19. Electrical resistivity of β'-$(ET)_3(GaCl_4^-)_{2-x}$-$(CoCl_4^{2-})_x$.[7]

the resulting β'-$(ET)_3(FeCl_4^-)_{0.80}(CoCl_4^{2-})_{1.20}$ shows a ferrimagnetic increase of χT, followed by a magnetic transition around 3 K.[184]

A similar doping of the divalent anion $CoCl_4^{2-}$ to the 1:1 metallic compound $(TTM\text{-}TTP)FeBr_{1.8}Cl_{2.2}$, has been attempted.[8] The resulting doped compounds, listed in Table 7, are isostructural to the parent uniform compound, and the band filling is changed from the half filling $(TTM\text{-}TTP^+)$ to the zero filling $(TTM\text{-}TTP^{2+})$. As shown in Figure 20, the resistivity gradually increases with increasing donor charge, and the zero filling compound $(TTM\text{-}TTP)\text{-}Mn_{0.1}Co_{0.9}Cl_4$ is an insulator even at room temperature. The conducting behavior seems to change continuously from the half filling to the zero filling, and the most conducting compound is the parent half-filled compound.

The group at Angers University has succeeded in controlling the donor charge by using metal cluster anions, $[Re_6S_{8-n}Cl_{6+n}]^{n-4}$ $(n = 1-4)$.[185] The formal charge of Re is $3+$, and six Re atoms make an octahedron. In $[Re_6S_8Cl_6]^{4-}$, eight S atoms attach onto the edges of the octahedron, and six Cl atoms are bonded to the Re atoms. Some of the S^{2-} atoms are changeable to Cl^- by keeping the molecular structure, resulting in clusters with $4-$ to neutral charges. A considerable number of radical-cation salts with these anions are known (see Table 4).[121,186] Recently salts of unsubstituted BDT-TTP were prepared (Table 9). The parent compounds are $(BDT\text{-}TTP)_6[Re_6S_6Cl_8]$-$(TCE)$ and $(BDT\text{-}TTP)_8[Re_6S_7Cl_7](CH_2Cl_2)$, where the 6:1 and 8:1 compositions come from the unit cell containing one anion and respectively six and eight donor molecules. Thus, the donor charges are $1/3+$ and $3/8+$. Similarly to the cases of other BDT-TTP salts, the donor charge tends to be less than that giving a quarter filling.[187] When $[Re_6S_6Cl_8]^{2-}$ and $[Re_6S_7Cl_7]^{3-}$ are mixed, a compound with the intermediate composition, $(BDT\text{-}TTP)_7[Re_6S_6Cl_8]_{0.5}$-$[Re_6S_7Cl_7]_{0.5}(CH_2Cl_2)$, is obtained. Although the 7:1 composition comes from the crystal structure, the anion is a random mixture of the two anions, and
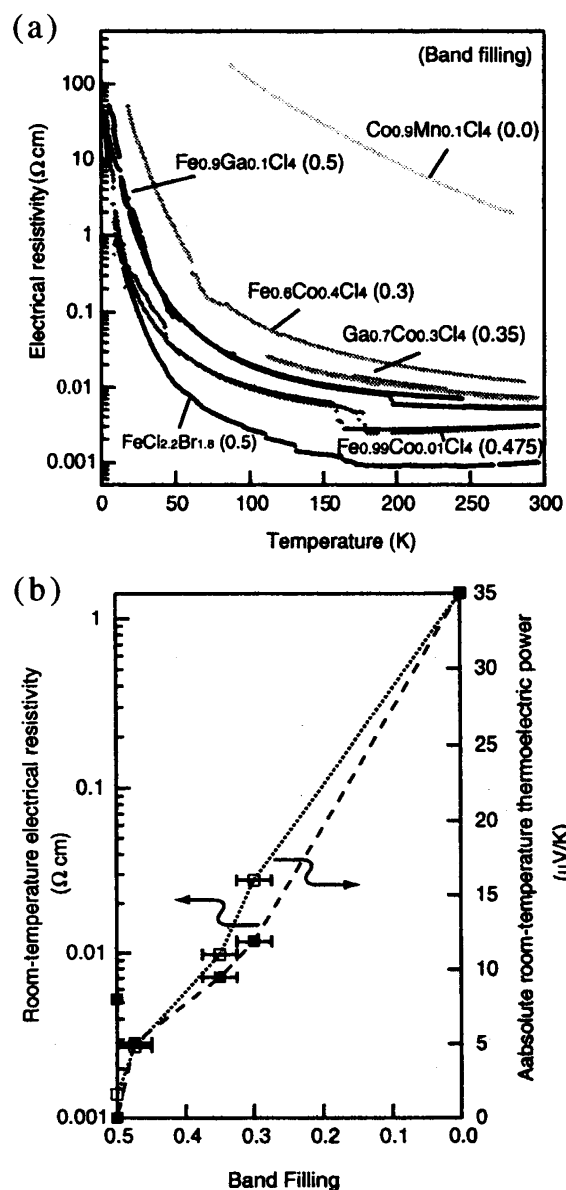
Figure 20. Electrical resistivity of alloyed TTM-TTP compounds (Table 7):[8] (a) temperature dependence of the electrical resistivity; (b) room-temperature resistivity and thermoelectric power as a function of the band filling.

the approximate 0.5 composition is determined from the chemical analysis (EDS). However, the resulting composition is just the sum of the two parent compounds. It is notable that all these compounds have β-type stacks with two-dimensional band structures, similarly to the cases of other BDT-TTP salts, and all compounds are basically metals down to low temperatures.

6.4. (DMeDCNQI)$_2$Li$_{1-x}$Cu$_x$

Another kind of carrier doping has been achieved in $(DMeDCNQI)_2Li_{1-x}Cu_x$ (DMeDCNQI = dimethyl-N,N'-dicyanoquinonediimine).[188] The original $(DMeDCNQI)_2Li$ undergoes a (spin-) Peierls transition at 60 K,[189] whereas $(DMeDCNQI)_2Cu$ is a metal down to low temperatures, because the mixed valent $Cu^{1.33+}$ mediates interchain interactions. When Cu is mixed with Li, the clear insulating state is lost above $x > 0.14$, and an entirely metallic state appears

Table 9. BDT-TTP Salts of $[Re_6Q_{8-n}Cl_{6+n}]^{n-4}$ (Q = S and Se; $n = 1-4$)[162b]

compound[a]	charge	conductivity[b]	structure	ref
(BDT-TTP)$_6$[Re$_6$S$_6$Cl$_8$](TCE)	0.333+		β	185
(BDT-TTP)$_6$[Re$_6$Se$_6$Cl$_8$](TCE)	0.333+	M	β	185
(BDT-TTP)$_7$[Re$_6$S$_6$Cl$_8$]$_{0.5}$[Re$_6$S$_7$Cl$_7$]$_{0.5}$(CH$_2$Cl$_2$)	0.357+	M	β	185
(BDT-TTP)$_7$[Re$_6$Se$_6$Cl$_8$]$_{0.5}$[Re$_6$S$_7$Cl$_7$]$_{0.5}$(CH$_2$Cl$_2$)	0.357+	M	β	185
(BDT-TTP)$_8$[Re$_6$S$_7$Cl$_7$](CH$_2$Cl$_2$)	0.375+	M	β	185

^{a} TCE = 1,1,2-trichloroethane ^{b} M = metals down to helium temperatures.

above $x > 0.39$.[190] At the same time, the drops of the magnetic susceptibility and NMR $(T_1T)^{-1}$ are wiped out.[190] In the insulating region ($x < 0.29$), a remarkable split of the C=N stretching mode is observed in the Raman investigation, indicating the presence of charge density waves, but this also disappears in the metallic region.[191] The same experiment demonstrates the actual change of the negative charge on the DMeDCNQI molecules. In this system, the alloying is possible over the entire region $0 < x < 1$, where the DMeDCNQI charge changes from 0.5− to 0.67−. Although the suppression of the MI transition is not due to the carrier doping itself but rather due to the three-dimensionality mediated by Cu, this is a most successful filling control in organic conductors. This system is also the only acceptor-type conductor appearing in the present review.

DMDCNQI
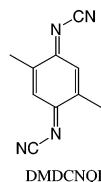
6.5. τ-Phase Salts

A series of characteristic compounds called "τ-phase", such as τ-(P-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$, are also nonstoichiometric conductors (P-S,S-DMEDT-TTF = pyrazino-S,S-dimethylethylenedithiotetrathiafulvalene).[192] The right half of this donor

P-S,S-DMEDT-TTF   EDO-S,S-DMEDT-TTF
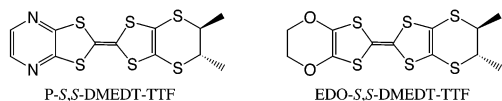
contains two chiral carbons in the dimethyl parts. This unit is included in dimethyl-ET, which is optically active, and (dimethyl-ET)$_2$AuI$_2$ is superconducting. But (dimethyl-ET)$_2$AuI$_2$ of the racemic donor is not superconducting.[193] The left half of P-S,S-DMEDT-TTF contains a pyrazine part, but a donor involving an ethylenedioxy part (EDO-S,S-DMEDT-TTF = ethylenedioxy-S,S-dimethylethylenedithiotetrathiafulvalene) also forms salts of τ-phase. Because these names are too long, P-S,S-DMEDT-TTF and EDO-S,S-DMEDT-TTF are sometimes abbreviated as NN and OO, respectively.

The τ-phase salts crystallize in a tetragonal system; this is the origin of "τ", where the donors are arranged perpendicular to each other surrounding the incorporated AuBr$_2$ anions (Figure 21a). In addition to this donor sheet, the anion sheet contains AuBr$_2$ anions parallel to the sheet. From the structure analysis, the anion sheet has 25% deficiency, so that the

(a)

(b)
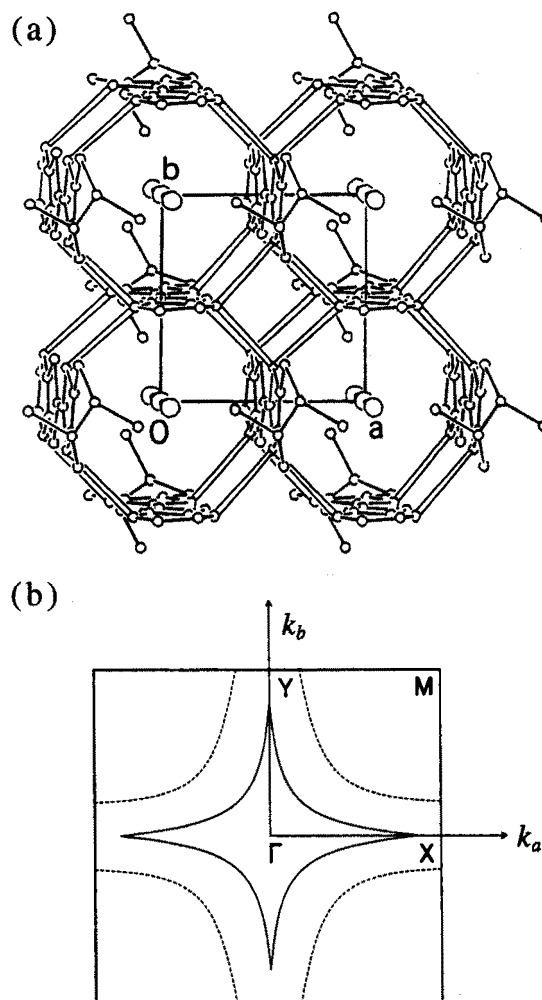
Figure 21. (a) Donor sheet structure and (b) the Fermi surface of τ-(P-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$.[192] The solid curve corresponds to $y = 0.75$, and the dotted curve is for $y = 0.0$ (the quarter filling).

composition is $y = 0.75$ in τ-(P-S,S-DMEDT-TTF)$_2$-(AuBr$_2$)$_{1+y}$. From this y, the donor has 0.875+ charge. Since the band filling is close to the half filling, the Fermi surface consists of a "starlike" pocket, whose cross section is 12.5% of the first Brillouin zone (Figure 21b). This kind of anion-incorporated sheet is in common with such compounds as δ- to ζ-phases of ET iodides (Table 2) and (ET)AuCl$_2$ (Table 4), and this structure usually leads to electrical insulators. There is, however, considerable intermolecular interaction between the perpendicular molecules. The anion deficiency is also crucial to the metallic conduction. Other linear anions form isostructural metallic salts,[194] but the AuBr$_2$ salts are mainly investigated both for the NN and OO donors.

The resistivity shows basically metallic behavior but increases below 50 K.[195,196] In this semiconducting region, however, very large negative magnetoresistance is observed, and the resistance increase is largely suppressed under a magnetic field of 5−10 T (Figure 22).[197] Furthermore, in the OO
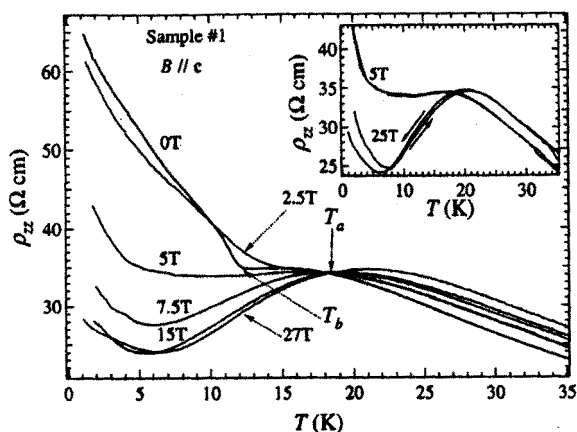
Figure 22. Temperature dependence of τ-(P-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ under magnetic fields. Reprinted with permission from ref 197. Copyright 2001 American Physical Society.

compound, when the magnetic field is rotated within the conducting plane, the angular dependence of the magnetoresistance has a tetragonal (90°) symmetry at 5 T but a 180° symmetry at 0.5 T (Figure 23).[195] This unusual angular dependence is explained if ferromagnetically aligned spins rotate together with the magnetic field at 5 T, but the magnetic order is pinned at 0.5 T. Weak ferromagnetism below 20 K has been suggested from the susceptibility measurement of the OO compound.[198] From the NMR measurements, the NN compound is reported to have an antiferromagnetic order below 20 K, but the OO compound has only a short range order.[199] Since this compound is close to the half filling, the possibility of ferromagnetism in a flat band has been theoretically suggested.[200] On the other hand, from the optical investigation, the unusual temperature dependence of the low-lying electronic excitation is attributed to a weak electronic localization effect.[201]

The observation of the Shubnikov−de Haas oscillations indicates the presence of small pockets that are 6.8% and 2.4% of the first Brillouin zone for the NN compound[170] and 6.1% and 0.66% for the OO compound (Figure 24).[202,203] Although the origin of the very small pockets is unclear, the 6.8% and 6.1% Fermi surface is about half of the estimation from the chemical analysis (12.5% in Figure 21). The observed Fermi surface corresponds to the compositions $y = 0.874$ and 0.898, respectively. It is notable that the observed Shubnikov−de Haas oscillations are anomalously large and are close to the quantum limit (the 22 T peak in Figure 24 corresponds to the second Landau level ($n = 2$)), because the Fermi surface is very small. Above 36 T, the resistance increases orders of magnitude with considerable hysteresis, and the system enters a new field-induced insulating phase.[204]
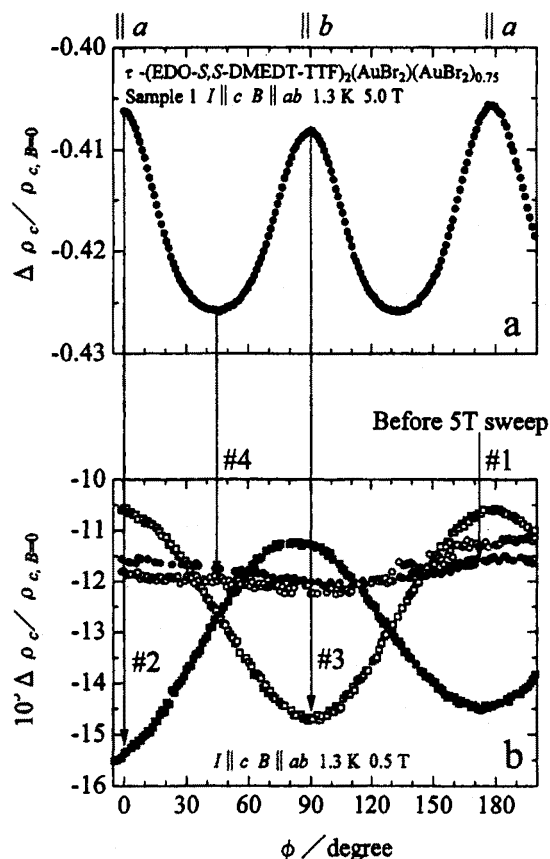
Figure 23. Angular dependence of the magnetoresistance of τ-(EDO-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$ at 1.3 K for I//c and B//ab at (a) 5 T and at (b) 0.5 T. Before the field sweep at 5 T, the angular dependence is small, as shown in #1 in part b. The field sweep at 5 T shows 90° symmetry, as shown in part a. Then the field is decreased from 5 to 0.5 T, and the angular dependence shows 180° symmetry, as shown in part b, but the position of the peak depends on the angle at which the field is decreased: #2 at 0° and #3 at 90°. When the field is decreased at 45°, #4 shows a very small angular dependence. Reprinted with permission from ref 195. Copyright 1999 The Physical Society of Japan.
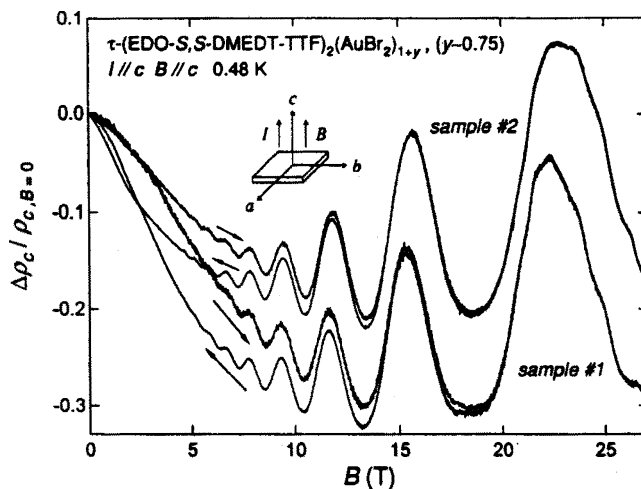
Figure 24. Shubnikov−de Haas oscillations in τ-(EDO-S,S-DMEDT-TTF)$_2$(AuBr$_2$)$_{1+y}$. Reprinted with permission from ref 202. Copyright 2002 American Physical Society.

6.6. MDT-TSF Salts

A nonstoichiometric compound (MDT-TSF)(AuI$_2$)$_{0.436}$ shows superconductivity at $T_c = 4.5$ K at ambient

pressure.[9] The donors construct uniform columns, and the anions form linear chains parallel to the donor columns (Figure 25). The X-ray oscillation
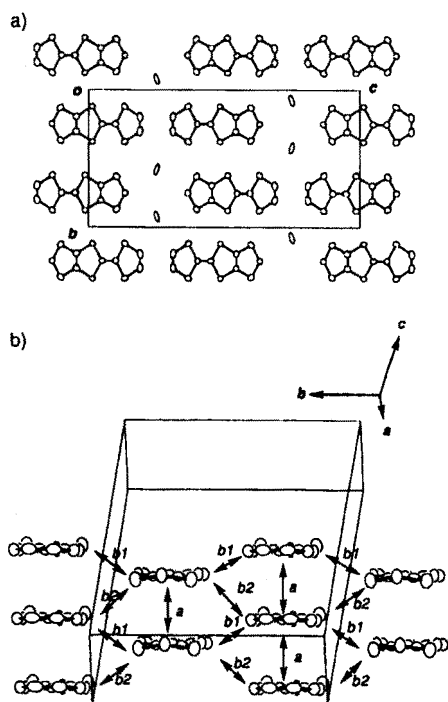
Figure 25. Crystal structure of $(MDT-TSF)(AuI_2)_{0.436}$.[9]

photograph shows complicated incommensurate layers similar to those in Figure 18. From the ratio of the donor sublattice, $a = 4.016$ Å, and the anion sublattice, $a' = 9.221$ Å, the composition is determined to be $a/a' = 0.436$.[205] Then the structural concept resembles $(TTF)X_x$ and $(TTM-TTF)I_{2.47}$. The electronic structure is, however, two-dimensional, owing to the enhanced interchain interaction, so that the Fermi surface is closed (Figure 26) and the metallic conductivity is maintained down to low temperatures. The closed Fermi surface is actually detected by the Shubnikov–de Haas oscillations and the angle-dependent magnetoresistance oscillations, even including the reconstruction due to the anion incommensurate potentials (Figure 26),[206] It is noteworthy that the Fermi surface reconstruction occurs according neither to the original incommensurate potential q nor to the weak one $2q$, but according to the most strong potential, $3q$.

The salts of this donor with linear anions, $(MDT-TSF)X_x$ ($X = I_3$, $I_{3-\delta}Br_\delta$, and $I_{3-\delta}Cl_\delta$), are isostructural and ambient-pressure superconductors at $T_c = 4.0-5.5$ K (Table 6).[10] The transition temperature is correlated with neither the anion length nor the lattice volume, whereas T_c is scaled by the lattice constant of the donor stacking axis. The sulfur analogue MDT-ST also forms isostructural superconductors (MDT-ST = $5H$-2-(1,3-dithiol-2-ylidene)-1,3-diselena-4,6-dithiapentalene).[144] It is notable that the all-sulfur analogue MDT-TTF and the all-selenium analogue MDSe-TSF form stoichiometric superconductors, κ-$(MDT-TTF)_2AuI_2$ and κ-$(MDSe-TSF)_2Br$ (T_c = 3.5 and 4 K, respectively) (MDT-TTF = methyl-
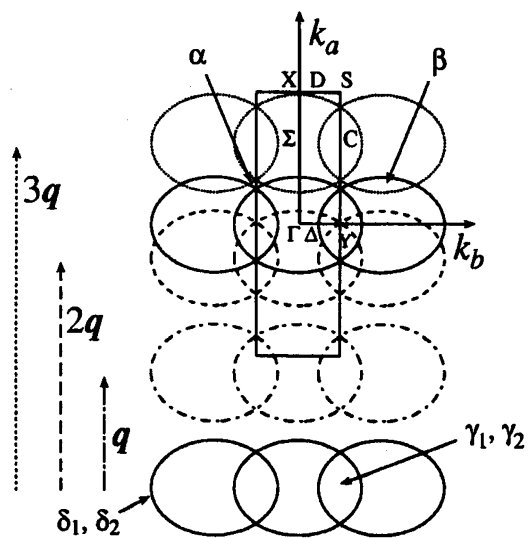
Figure 26. Reconstructed Fermi surface of $(MDT-TSF)$-$(AuI_2)_{0.436}$ in the $a*b*$ plane, translated by the incommensurate anion periodicities q, $2q$, and $3q$. The first Brillouin zone is that from the donor lattice. The observed Shubnikov–de Haas oscillations correspond to the original Fermi surface (δ), the overlapped area (γ), and those reconstructed by the incommensurate anion potential $3q$ (α and β). Reprinted with permission from ref 205. Copyright 2002 American Physical Society.

enedithio-TTF, and MDSe-TSF = methylenediselenotetraselenafulvalene).[207]

MDT-ST   MDT-TTF   MDSe-TSF
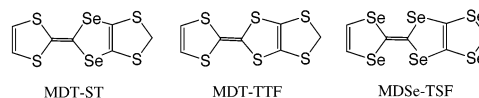
7. Summary

Before summarizing the unusual band fillings, we have to examine how the compositions of radical-cation salts are determined. A simple example is $(MDT-TSF)(AuI_2)_{0.436}$, where the ratio of the donor spacing and the anion length determines the nonstoichiometric composition. This principle is generally applied to many nonstoichiometric compounds such as $(TTF)X_x$ and $(TTM-TTF)I_{2.47}$. This principle is valid when the donors construct uniform columns.

In stoichiometric compounds, we have found the tendency that the charge on ET is apt to exceed the quarter filling, whereas BO prefers a 0.4+ charge. This is not accounted for from the redox potentials. Redox potentials are usually not recognized as an important factor to determine the composition. In general, donors with four methylthio groups, such as TTM-TTF and TTM-TTP, have a strong tendency to realize highly oxidized states; examples are $(TTM-TTF)(I_3)_{0.823}$, $(TTM-TTP)I_3$, and $(TTM-TTP)(I_3)_{5/3}$ (Figure 27). The sides of these donors are blocked with the extending methylthio groups, and anions come to the sides of these donors, instead of the ends of the donors. This seems to be the reason for the large anion content of these salts. This is, however, the origin of the high one-dimensionality of these compounds as well. We have recently found that when the ethylenedithio part of ET is chlorinated, the large steric effect of the resulting donor gives rise to 1:1
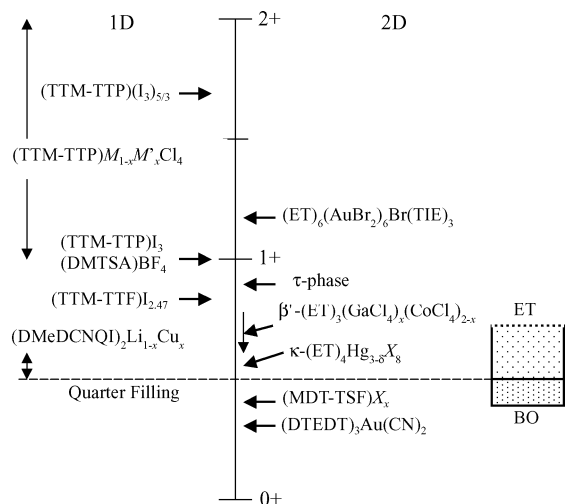
Figure 27. Summary of the compounds discussed in this review, plotted against the donor charge.

compounds, though the donor ability is considerably reduced.[208] Probably the large anion content of the τ-phase is also related to the methyl groups of the donors. These structural factors are the principal origin of the unusual band fillings.

Preparation conditions are also an important factor to determine the composition of the final product. The direct reaction with iodine leads to high oxidation states (Table 2), in which the anion is sometimes incorporated in the donor sheet. The conducting properties of such anion-incorporated compounds are usually poor, though there are several important exceptions such as $(TTM\text{-}TTP)(I_3)_{5/3}$ and the τ-phase. The use of polyvalent anions in the electrocrystallization usually results in high oxidation states. For example, in the case of mercury halides, the usual anion $HgBr_3^-$ brings about $(ET)_3(HgBr_3)_2$ or $(ET)\text{-}HgBr_3$, and addition of $HgBr_2$ to $HgBr_3^-$ is necessary to obtain the nearly quarter-filled $(ET)_4Hg_{2.89}Br_8$. The use of $HgBr_4^{2-}$ leads to $(ET)_5Hg_3Br_{11}$, where if the charge is averaged over all ET molecules, the donor charge is 1+.

Many of the highly conducting radical-cation salts with unusual band fillings have uniform one-dimensional columns, but the ground states of these one-dimensional compounds are nonmagnetic Peierls-like states. Examples are $(TTF)X_x$, $(TTM\text{-}TTF)I_{2.47}$, $(TTM\text{-}TTP)I_3$, and $(DMTSA)BF_4$. Thanks to the TTM-TTP compounds, high oxidation states are well explored for one-dimensional systems (Figure 27). There are, however, very few two-dimensional compounds except for $(DTEDT)_3Au(CN)_2$ and $(MDT\text{-}TSF)X_x$. Although these compounds have uniform columns, the Fermi surface is closed, and the electronic structures are two-dimensional. These compounds maintain metallic conductivity down to low temperatures and exhibit superconductivity.

In connection with the universal phase diagrams of organic conductors, the remaining issues are (1) what are the mechanism and symmetry of superconductivity in the superconductors bordering on nonmagnetic insulating states and (2) is the half filling or the quarter filling a singularity in organic conductors. As for issue 1, the TMTSF family and the

κ-phase ET compounds have a series of compounds including ambient-pressure superconductors, and investigations of superconductivity are possible under ambient pressure. For nonmagnetic compounds, however, such an ambient superconductor is not obtained. As for issue 2, the carrier doping to TTM-TTP (Figure 20) seems to indicate that the half filling is not a singularity. In this case, however, the competing instability is the Peierls instability. The number of metallic two-dimensional systems is insufficient, and filling control in two-dimensional systems is still very limited. Future progress in this direction will largely depend on the development of new materials.

8. Acknowledgments

9. References

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