Study on Synthesis and Characterization of New Synthetic Metals and Superconductors Based on Planar π-Conjugated Molecules

平面 π-共役系から構築される
分子性金属・超伝導体の開発に関する研究

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Study on Synthesis and Characterization of New Synthetic Metals and Superconductors Based on Planar π-Conjugated Molecules

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Toshio Saito

……we think, in concluding that the organic radicals in our amalgams are in the metallic state and, therefore, that it is possible to prepare composit metallic substances from non-metallic constituent elements—H. N. McCoy and W. C. Moore, *J. Am. Chem. Soc.*, **33**, 273(1911).

……From a realistic estimation of the matrix elements and density of states in this polymer it is concluded that superconductivity should occur even at temperatures well above room temperature.—W. A. Little, *Phys. Rev.*, **134**, A1416(1964).

I wish to draw attention to the potential of odd alternant hydrocarbons (OAHs) in the design of organic metals and superconductors which gives reason to suppose that they may prove equal or even superior to present systems.……—R. C. Haddon, *Nature*, **256**, 394(1975).

Contents

Chapter 1.

General Introduction

1-1. Molecular-Based Materials

Material Science towards 21st Century

As illustrated with such names as the Stone Age, the Bronze Age and the Iron Age, human history has long been accustomed to watch the evolution of the material which mankind has got in hand. However, the last quarter of 20th century might be astonished and bewildered to witness an outburst of new materials. In September 1986, Bednorz and Müller broke some 14 year stagnation of raising the critical temperature (T_c) by reporting "Possible high T_c superconductivity in the Ba-La-Cu-O system" [1 (a)]. Shortly thereafter Chu *et al.* broke the record by finding 90-K superconductivity in the Y-Ba-Cu-O system, which set fire to a worldwide search for even-higher-temperature superconductors. Thereafter a series of cuprates has been found to conduct electricity with a "zero-resistance" state one after another and T_c skyrocketed toward room temperature within a few years [1] (see Figure 1.2).

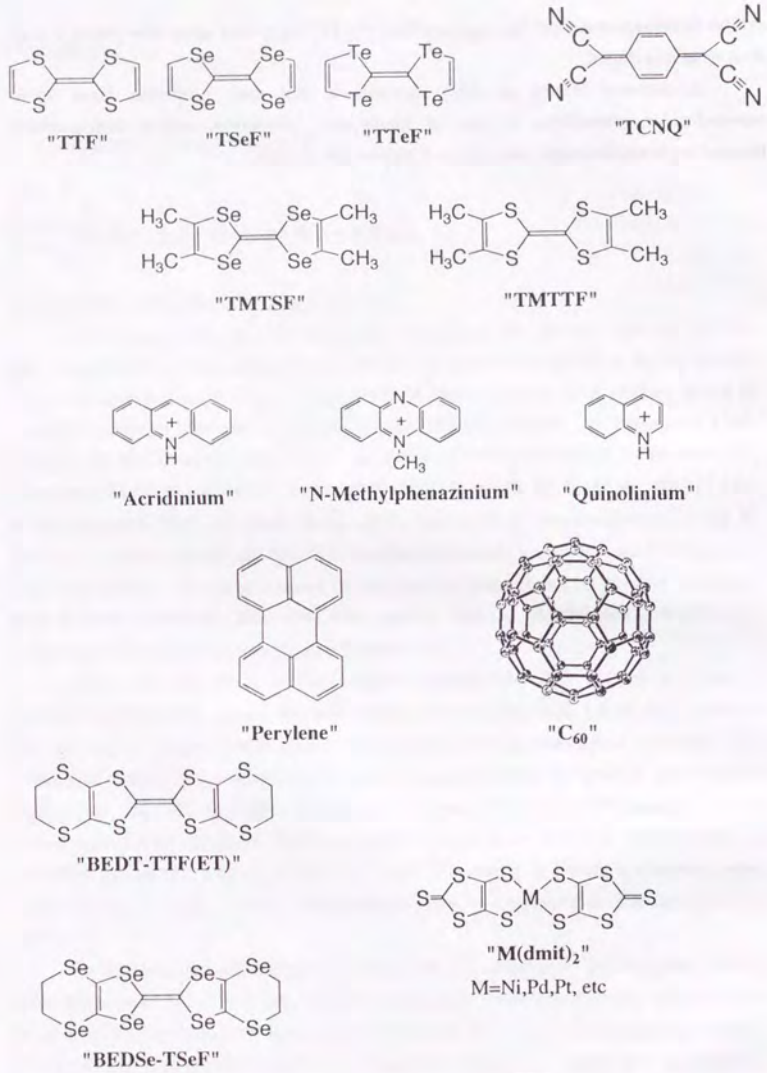
More than ten years before, organic compounds also became a focus of contemporary material science research mainly due to their well established synthetic methodologies. However few people had dreamed of an appearance of a metallic one, which was realized in a certain kind of organic charge transfer complex in 1973 [2] (cf. Figure 1.4). In 1979 an organic selenium compound attracted world's attention, for its radical salts turned out to be the first organic compound to exhibit a superconducting transition [3 (a)] (cf. Figures 5 and 6). The following two years, researchers were excited at succesive discoveries of superconductivity in a series of related salts [3] (see Table 1.1).

In the meantime, some organic polymers were claimed to be ferromagnets even at room temperature in late 80's [4]. In 1991 a polymeric vanadium complex was found to be attracted to a permanent magnet up to the thermal decomposition temperature of it (> 350 K)[4 (g), (h), (i)] (see Figure 1.3). Yet still few researchers might have the slightest idea that the first simple and well-defined organic radical ferromagnet would coincide with it [5].

Now a soccer-ball-shaped all-carbon macromolecule or rather a carbon cluster, C_{60}, extracted from carbon soot, is highlighted for potentially wide applications in addition to its peculiar shape and preparation method; for example it has been shown to

exhibit ferromagnetism [6] and superconductivity [7] depending upon how heavily and with what it is doped.

A common feature of these materials is that their properties base upon intermolecular interactions instead of interatomic interaction, which distinguishes themselves from elemental materials such as mercury or iron.



Scheme 1.1. Components of molecular conductors

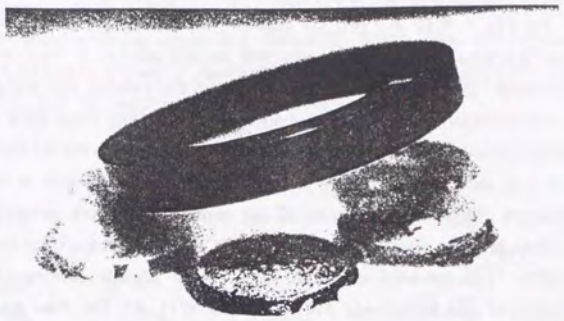


Figure 1.1. A magnet ring levitating over high-T_c copper oxide superconductor pellet samples (Meissner effect) after immersion in liquid nitrogen. From ref. [37].

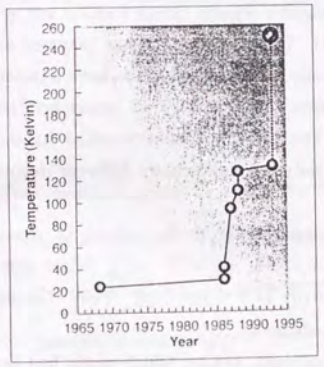


Figure 1.2. Record of high-T_c superconductivity critical temperature (T_c) versus year. From ref. [38], which excitedly reports French researchers' latest observations of sustained superconductivity at temperature as high as 250 K—a jump of more than 100 K from the previous best. See also Figure 1.7.

Figure 1.3. Photograph of a powdered sample of the $[V(TCNE)_x]\cdot y(CH_2Cl_2)$ magnet being attracted to a Co_5Sm magnet. From ref. [4 (i)].

Organic Conducting Materials

Thanks to the diversity, organic compounds have always played an important role in the progress of material science. When superconductivity was first discovered in 1911 in elemental Hg (T_c = 4.15 K) [8], by coincidence, during the same year it was speculated that "it is possible to prepare composite metallic substances from non-metallic constituent elements." [9] Thus, the notion of a material that exhibits increasing electrical conductivity with decreasing temperature but does not contain any metal atom was born. At first, organic semiconductors appeared in 1940's though they were far from metallic ones and there were still more than thirty years to wait before a real burst in research on organic conductors did occur. A history of the organic conductors dawned in 1954, when the perylene-bromine complexes were found to exhibit high electrical conductivity (~ 1 – 10^{-1} Scm^{-1}; an extraordinary high value for an organic compound then) by Akamatsu, Inokuchi and Matsunaga [10]. In late 60's the Du Pont group, who synthesized a variety of salts of a new mighty acceptor named tetracyanoquinodimethane (TCNQ), found that N-methylphenazinium·TCNQ, quinolinium·$(TCNQ)_2$ and acridinium·$(TCNQ)_2$ were the first metallic organic compounds in narrow region around room temperature [11]. Another important compound is tetrathiafulvalene (TTF), which was synthesized and found to form highly conductive radical cation salts in 1970 [12]. From the viewpoint of electrical conductivity, one of the early epochs worthy of mentioning in particular is the appearance of a metallic organic charge transfer salt with "giant conductivity": TTF-TCNQ [2] (Figure 1.4). This compound, when prepared as a single crystal, exhibits a high anisotropy; practically, it has turned out to have a metallic conductivity exclusively along a particular direction. This is why the researchers later have come to call it as a one-dimensional metal. The following studies revealed that there are variety of related compounds that exhibit slightly but significantly different electrical properties.

On the other hand, some kind of polymers added to the interest in organic compounds. Superconductivity was found in $(SN)_x$ in 1975 [13], while doped polyacetylene $(CH)_x$ exhibited as a high conductivity as 5×10^2 Scm^{-1} [14]. Graphite intercalation compounds also showed metallic conductivity.

The news that now not a few organic materials, against which many had been prejudiced as typical insulators, showed metallic conductivity did stimulate not only physists but also chemists. Ever since, with the aid of expectation of potential superconductivity propounded by some theoreticians [15], which was combined with erroneous suggestion that TTF-TCNQ might indicate a possibility of high-temperature supercondictivity [16], chemists have made every effort to synthesize similar salts as well as those of related donor or acceptor molecules, while physists have made various measurements to elucidate their unusual transport, optical and magnetic properties one after another. New compounds led to a finding of new physical phenomena such as

Peierls instability [17], charge density waves and spin density waves [17, 18] and would often cast further questions at the same time. In this way an increasing number of chemists, physists and theoreticians have entered the field, which now involves a wide variety of materials from inorganic to organic molecules, from molecules to clusters. The research of such artificial conducting materials, which they call synthetic metals (synmetals), molecular metals or organic metals and superconductors, has grown out of merely a boom to a new scientific area.

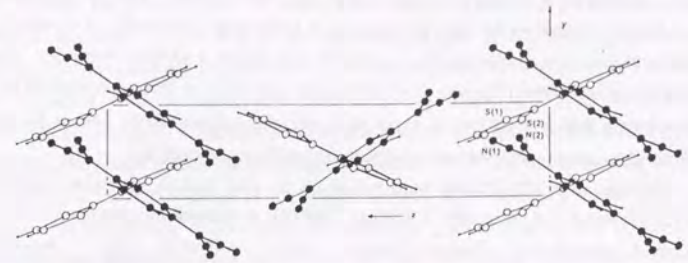


Figure 1.4. Side- (down [100]) views of the crystal packing in TTF-TCNQ. The TTF and TCNQ molecules stack to form each segregated column along y axis, from ref. [2 (b)].

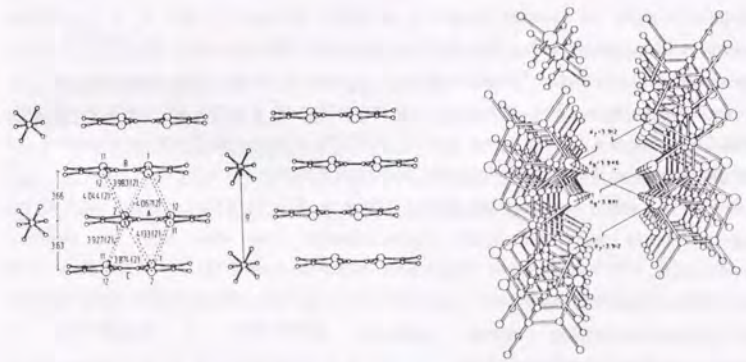


Figure 1.5. (Left-hand) Side-view of stacks (tilted 10 °) showing shorter distances (Se—Se) (Å) within a stack; and view along *a* showing shorter interchain distances (Se—Se and Se—F) (Å) of the first superconducting organic solid $(TMTSF)_2PF_6$, from ref. [3 (g)]
(Right-hand) View down the stacking direction in $(TMTSF)_2BrO_4$, from ref. [46]

1-2. Planar π-conjugated Donor Molecules Including Sulfur and/or Selenium Atoms on the Periphery

Low-dimensional Metals and Superconductors

From the study of TTF-TCNQ and other one-dimensional metals, it dawned upon many scientists that such metals are intrinsically unstable as Peierls predicted [17] and that superconducting state is one of some possible ground states of one-dimensional metals. It had been commonly agreed that we should know how to increase an intermolecular interaction, in other words, how to increase dimensionality of an electronic structure, to suppress a metal-insulator transition and achieve a superconductivity. Some leading group felt around for this goal towards an extension of the π-conjugation in the TTF molecule, which effect can be expected to enhance a donor ability and, at the same time, to reduce an on-site Coulomb repulsion with a large polarizability.

7 years after TTF-TCNQ there turned up the first organic superconductivity in $(TMTSF)_2PF_6$ at 1.4 K under 6.5 Kbar (TMTSF = tetramethyltetraselenafulvalene; $\Delta^{2,2'}$-bi-4,5-dimethyl-1,3-diselenolylidene) [3], followed by successive superconductivities found in related organic solids at moderate hydrostatic pressures of 1.2 GPa in the 0.4 – 1.5 K region [19]. In these materials the donor (TMTSF) molecules stacks to make one-dimensional columns as TTF salts, but intermolecular Se---Se contacts observed between two stacks as well as in a stack strengthen the intercolumnar interaction enough for pressure, which adds intermolecular interaction a little more, to suppress a metal to insulator transition occurring between 10 and 20 K at ambient pressure. Because of such a little but significant two-dimensionality the TMTSF salts, which are often referred as "Bechgaard salts", have come to be called quasi-one- or low-dimensional systems [20]. Owing to the availability of a series of isostructural salts including those of a similar donor TMTTF (TMTTF = tetramethyltetrathiafulvalene), the unique physics of the low-dimensional conductors was brought to light. Yet the low T_c (0.4 – 2.1 K) and if necessary the high pressure (~ 8 – 12 Kbar) prevent most of the experiments to probe the actual superconducting state other than the electrical conductivity, which drove many researchers' interest to raising the T_c. Then there came an excellent successor; noticeable improvement in T_c was obtained with some salts of non-selenium-containing donor molecule BEDT-TTF { BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene; 5,5',6,6'-tetrahydro-2,2'-Bi-1,3-dithiolo[4,5-b][1,4]dithiinylidene } but the enhancement of T_c is not all about what BEDT-TTF has offered.

BEDT-TTF Salts

This donor molecule, often abbreviated as ET, was originally synthesized by M. P. Cava and coworkers [21] and several improved or modified methods have been reported [22]. One of the important differences between ET system and previous systems lies in the general tendency toward two dimensional packing mode of the ET molecule [23], while the others has a trend to a one-dimensional stack. In this context, the preparation of $ET_2ClO_4(C_2H_3Cl_3)_{0.5}$ [23 (d)] and ET_2PF_6 [23 (b), (c), (e)] were important historical steps in the study of ET salts. Its X-ray crystal structural analysis demonstrated, for the first time, the ability of the donor to compose a two-dimensional electronic structure. Since then all the following scores of ET salts supported this tendency, emphasizing and impressing the versatile properties of the donor as a building block for stable metals and superconductors. In fact, in contrast to TMTSF and TMTTF, ET salts often crystallize in multiple phases but a number of intermolecular short contacts between sulfur atoms within van der Waals distance (3.70 Å) are found in most of them irrespective of the size or shape of the counter anions. The molecular feature that both terminal ethylene groups deviate from the molecular plane might be the predominant reason for non-stacking structure of ET salts and thus their unique properties. After the first superconductivity of this class was found in $(BEDT\text{-}TTF)_2ReO_4$ in 1983 [24], ET has recorded many highs one after another; it has produced the largest number of (nearly 30) superconductors [25, 42] including the one with the highest T_c (the $Cu[N(CN)_2]Cl$ salt, 12.8 K under 0.3 Kbar [25 (a)]) in organic superconductors (Table 1.1), the largest number of (more than 100) metallic charge transfer salts, the richest variety of the crystal structures (α-, α'-, α_t-, β-, β'-, β"-, β^*-, γ-, γ'-, δ-, ε-, ζ-, η-, θ-, κ-, λ-, t- and m-types in addition to unnamed ones), innumerable kinds of salts and thus the most reports from brief communications to a 150-page review. As a result, on this ET system abundant studies and a variety of data have been accumulated from all over the world [26]. In a sense it was fortunate for the researchers of the field that the TMTSF salts came first then ET salts instead of vice versa; otherwise they could be confused by the diverse and complicated structures and properties of the ET system.

Table 1.1. Organic superconductors and their critical temperatures

Compound	$T_c^{\dagger}$ (K)	reference(s)
	TMTSF compounds	
$(TMTSF)_2PF_6$	0.9 K (1.2 GPa)	[3(a)]
$(TMTSF)_2AsF_6$	1.1 K (1.2 GPa)	[3(c)]
$(TMTSF)_2SbF_6$	0.4 K (1.1 GPa)	[3(d)]
$(TMTSF)_2TaF_6$	1.4 K (1.2 GPa)	[3(d)]
$(TMTSF)_2ClO_4$	1.3 K	[19 (f)], [3(d)]
$(TMTSF)_2ReO_4$	1.3 K (0.95 GPa)	[3(e)]
$(TMTSF)_2FSO_3$	2.1 K (0.65 GPa)	[3(f)]
	ET compunds	
$(BEDT\text{-}TTF)_4(ReO_4)_2$	2.0 K (0.45 GPa)	[24]
β_L-$(BEDT\text{-}TTF)_2I_3$	1.4 K	[25(b)]
β_H-$(BEDT\text{-}TTF)_2I_3$	8.0 K (0.05 GPa)	[25(c), (d)]
γ-$(BEDT\text{-}TTF)_3I_{2.5}$	2.5 K	[25(e)]
α_t-$(BEDT\text{-}TTF)_2I_3$	6–7 K	[25(f)]
	8 K	[25(g)]
κ-$(BEDT\text{-}TTF)_2I_3$	3.6 K	[25(h)]
θ-$(BEDT\text{-}TTF)_2I_3$	3.6 K	[25(i)]
β-$(BEDT\text{-}TTF)_2IBr_2$	2.8 K	[25(j)]
β-$(BEDT\text{-}TTF)_2AuI_2$	5.0 K	[25(k)]

Table 1.1. Organic superconductors and their critical temperatures (continued)

Compound	$T_c^{\dagger}$ (K)	reference(s)
κ-$(BEDT\text{-}TTF)_4Hg_{2.78}Cl_8$	1.8 K (1.2 GPa)	[25(l-1)]
	5.3 K (2.9 GPa)	[25(l-2)]
κ-$(BEDT\text{-}TTF)_4Hg_{2.89}Br_8$	4.3 K	[25(m)]
	6.7 K (0.35 GPa)	[25(n)]
$(BEDT\text{-}TTF)_2Hg_{1.41}Br_4$	2.0 K	[25(o)]
κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$	10.4 K	[25(p)]
κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$	11.6 K	[25(q)]
κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$	12.8 K (0.03 GPa)	[25(a)]
κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]CN$	10.4 K	[25(r)]
κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl_{0.5}Br_{0.5}$	11.3 K	[25(t)]
κ-$(BEDT\text{-}TTF)_2Ag(CN)_2{\cdot}H_2O$	5.0 K	[25(u)]
κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$	2.8 K (0.15 GPa)	[25(v)]
κ_L-$(BEDT\text{-}TTF)_2Cu(CF_3)_4{\cdot}TCE$	4.0 K	[42(a)]
κ_H-$(BEDT\text{-}TTF)_2Cu(CF_3)_4{\cdot}TCE$	9.2 K	[42(b)]
κ_L-$(BEDT\text{-}TTF)_2Ag(CF_3)_4{\cdot}TCE$	2.6 K	[42(c)]
κ_{H1}-$(BEDT\text{-}TTF)_2Ag(CF_3)_4{\cdot}TCE$	9.4 K	[42(c)]
κ_{H2}-$(BEDT\text{-}TTF)_2Ag(CF_3)_4{\cdot}TCE$	11.1 K	[42(c)]
α-$(BEDT\text{-}TTF)_2NH_4Hg(SCN)_4$	1.15 K	[25(w)]
α-$(BEDT\text{-}TTF)_2KHg(SCN)_4$	~0.3 K	[43]
$(BEDT\text{-}TTF)_3Cl_2{\cdot}2H_2O$	2 K (1.6 GPa)	[25(x)]
$(BEDT\text{-}TTF)_4Pt(CN)_4{\cdot}H_2O$	2 K (0.65 GPa)	[25(y)]
$(BEDT\text{-}TTF)_4Pd(CN)_4{\cdot}H_2O$	1.2 K (0.7 GPa)	[25(z)]

Table 1.1. Organic superconductors and their critical temperatures (continued)

Compound	T_c† (K)	reference(s)
	DMET compounds	
$(DMET)_2Au(CN)_2$	0.8 K (0.5 GPa)	[36(a)]
$(DMET)_2I_3$	0.47 K	[36(b)]
$(DMET)_2IBr_2$	0.59 K	[36(b)]
$(DMET)_2AuCl_2$	0.83 K	[36(c)]
$(DMET)_2AuI_2$	0.55 K (0.5 GPa)	[36(c)]
$(DMET)_2AuBr_2$	1.0 K (0.15 GPa)	[36(d)]
κ–$(DMET)_2AuBr_2$	1.9 K	[36(e)]
	M(dmit)2 compounds	
$TTF[Ni(dmit)_2]_2$	1.6 K (0.7 GPa)	[37(a) – (c)]
$Me_4N[Ni(dmit)_2]_2$	5.0 K (0.7 GPa)	[37(d) – (f)]
EDT-TTF[Ni(dmit)2]	1.3 K	[37(g)]
α'–$TTF[Pd(dmit)_2]_2$	6.42 K (2.07 GPa)	[37(h), (i)]
α–$TTF[Pd(dmit)_2]_2$	1.7 K (2.175 GPa)	[37(b), (h)]
β–$Me_4N[Pd(dmit)_2]_2$	6.2 K (0.65 GPa)	[37(j) – (l)]
$Me_2Et_2N[Pd(dmit)_2]_2$	4.0 K (0.24 GPa)	[37(k), (m)]

Table 1.1. Organic superconductors and their critical temperatures (continued)

Compound	T_c† (K)	reference(s)
	Other compounds	
κ–$(MDT\text{-}TTF)_2AuI_2$	4.5 K	[38(a)]
β_m–$(BEDO\text{-}TTF)_3Cu_2(SCN)_3$	1.06 K	[38(b)]
$(BEDO\text{-}TTF)_2ReO_4 \cdot H_2O$	2.5 K	[38(c)]
$(DMBEDT\text{-}TTF)_2ClO_4$	2 K (0.58 GPa)	[38(d)]
$(DMET\text{-}TSF)_2AuI_2$	0.58 K	[38(e)]
λ–$(BETS)_2GaCl_4$	8 K	[38(f), (g)]
λ–$(BETS)_2GaCl_3Br$	8 K	[44]
$(DTEDT)[Au(CN)_2]_{0.4}$	4 K	[45]
	C60 compounds	
K_xC_{60}	18 K	[7(a)]
K_3C_{60}	19.3 K	[7(c)]
Rb_xC_{60}	28 K	[7(f)]
Rb_xC_{60}	30 K	[7(c)]
$Cs_xRb_yC_{60}$	33 K	[7(e)]
Cs_xC_{60} (x = 1.2–3)	30 K	[7(d)]

†At ambient pressure in those entries where no pressure is indicated in parentheses. This Table does not include intercalate superconductors, *e.g.* T_c = 6.1 K for $SnSe_2\{Co(n\text{-}Cp)_2\}_{0.3}$ [41].

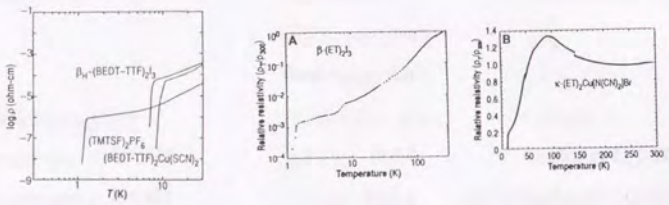


Figure 1.6. The superconducting transition in various organic conductors. $(TMTSF)_2PF_6$ is under 8 Kbar; both BEDT-TTF salts are at atmospheric pressure. From ref. [18 (f)] and [26 (e)]. For acronyms see Scheme 1.1.

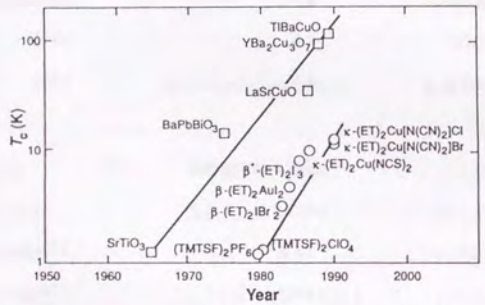
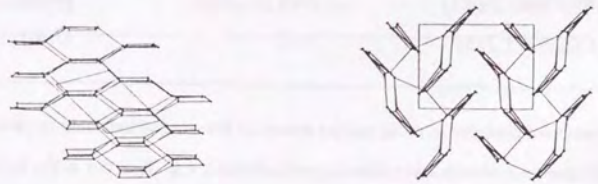


Figure 1.7. A plot of T_c versus year of discovery for inorganic oxide (square) and organic superconductors (circle). From ref. [26 (e)].



β−type κ−type

Figure 1.8. ET molecule network in β− and κ−type organic superconductors. Thin lines indicate short intermolecular contacts, and the unit cell boundaries are also indicated. From ref. [26 (e)]. Compare with Figure 1.5.

Beyond BEDT-TTF ("ET")

Syntheses and characterizations have been chiefly intended for understanding of such diversity; how a chemical modification of some molecule would affect the crystal structure and thus the property of the charge transfer salt by comparison of two similar salts. Therefore many of the researches in the molecular-based conducting materials centered around ET salts. Accordingly such chalcogen donor molecules other than ET and its unsymmetrical derivatives remain relatively unexplored, for example TSeF (TSeF = tetraselenafulvalene) derivatives. So far some studies demonstrated that introduction of selenium or tellurium atom(s) in the fulvalene moiety often results in an unexpected synthetic problem and substantial difference in the properties of the charge transfer salts [27], still little information is available on their cation radical salts and the crystal structures. In order to contribute to development of organic conductors, synthetic approach to new TSeF derivative donor systems is the main subject of this thesis.

1-3. M(dmit)$_2$ Systems

A Chalcogen Acceptor

Another indispensable organic solids is those of acceptors. The pursuit of a stable metallic and superconducting organic solid in the above-mentioned way had driven many researchers to pay much attention to the molecules containing more and heavier chalcogen atoms, for example from TTF through TSeF to TTeF (TTeF = tetratellurafulvalene) or BEDT-TTF to BEDSe-TSeF {BEDSe-TSeF = bis(ethylenediselena)-tetraselenafulvalene} in order to enhance an intermolecular interaction and to reduce an on-site Coulomb energy. On the other hand an acceptor molecule usually includes atoms with high electronegativities such as halogen, oxygen and nitrogen atoms. These atoms or strong electron-withdrawing groups often prevent intermolecular interaction for they do not have so spatially extended π-orbitals as chalcogen atoms do, in addition to their strong tendency to localize electrons around them. Therefore the development of acceptor conducting systems falls much behind that of donor systems. In such situaion, however, there are a unique group of compounds which have been anticipated to circumvent this problem and thus have drawn respectable attention for many years, *i.e.* metal complexes, particularly those of sulfur ligands. Owing to their unusually stabilized oxidation states of the metal ions, they have played an important role in development of solid state chemistry [28] and have appealed to wide and diverse interest in inorganic, bio- and analytical chemistry as well [29]. On the other hand, still a limited number of compounds could be formed based on [Pt(CN)$_4$] or [Pt(C$_2$O$_4$)$_2$] anions, all of which underwent a metal-to-insulator transition above 70 K [28 (j), (k)] due to the marked one-dimensional character.

Among such acceptor molecules M(dmit)$_2$ (M = Ni, Pd, Pt, Au, etc: dmit = dimercaptoisotrithione; 1,3-dithiole-2-thione-4,5-dithiolate) is only one that has produced molecular superconductors so far [30]. This system is unique in several respects;

— first, they are sufficiently stable acceptors without any atoms or function groups of high electronegativity,

— secondly, although they are classified into acceptors, they are easily oxidized to form a charge-transfer salts with large cations such as heavy alkaline atoms, onium ions and donor molecules,

— additionally, their molecular structures remind us of chalcogen donors like ET, therefore they can be considered to be an acceptor counterpart of chalcogen donors, or intermediates between donors and acceptors,

— fourthly, they can be also considered to be intermediates between inorganic and organic compounds, since they consist of central metal atoms and the organic ligand (dmit^{2-}), and

— fifthly, although the central metals do not play an important role in the molecular orbitals that are relevant to their solid state properties, the properties change sometimes drastically and sometimes delicately when we change the central metals.

As mentioned above, the dmit complex resembles ET molecules in that it also has many sulfur atoms on the periphery and actually sometimes take similar packing motif in the salts. Yet when it forms a charge transfer salt it exhibits different properties owing to its b_{2g} symmetry of the LUMO (LUMO = the lowest unoccupied molecular orbital), which is expected to make a valence band in the solids, while ET's HOMO (HOMO = the highest occupied molecular orbital), which is in turn expected to make a valence band in the solids, has a different symmetry [31]. The intermolecular interactions of side-by-side one usually almost cancell out each other and dmit-based conductors also often result in one-dimensional electronic structures [32].

There are, however, some exceptions worth referring to.

— First, the cases of strong dimerized palladium and platinum complexes, where the conduction bands mainly consist of HOMO of the complex molecules [33]. Because the HOMO of M(dmit)$_2$ has same symmetry as that of ET, it can also form a two-dimensional crystal and electronic structure based on short S---S contacts in the acceptor sheets as ET does in many salts.

— Secondly, the cases of the nickel complex with a characteristic packing motif called "spanning overlap" [34]. α-(CH$_3$)$_2$(C$_2$H$_5$)$_2$N[Ni(dmit)$_2$]$_2$, α-(C$_7$H$_{16}$N)[Ni(dmit)$_2$]$_2$ and γ-(CH$_3$)$_2$(C$_2$H$_5$)$_2$N[Ni(dmit)$_2$]$_2$ were report to have such packing arrangement that one molecule overlaps with two neighboring molecules. They all remain metallic down to the temperature lower than 4.2 K due to the two-dimensional electronic structures reminiscent of the κ-type ET salts.

— Thirdly, the cases of multi-Fermi surfaces [35]. The donor-acceptor type compounds TTF[Ni(dmit)$_2$], α-TTF[Pd(dmit)$_2$], α'-TTF[Pd(dmit)$_2$], EDT-TTF$_2$[Pd(dmit)$_2$]$_2$ and closed-shell cation salts (CH$_3$)$_4$N[Ni(dmit)$_2$]$_2$ and β-(CH$_3$)$_4$N[Pd(dmit)$_2$]$_2$ belong to this class, though some of them are not stable metals in low temperature at ambient pressure. Their common structural feature is that they have two independent stacking columns running different directions in the crystals. Accordingly they have two independent one-dimensional Fermi surfaces if the interaction between the two columns is negligible. Two Fermi surfaces can hardly disappear by a single modulation wave vector, *i.e.* the system resists CDW (CDW = charge density wave) [31].

These studies demonstrated a unique way to construct two-dimensional electronic systems based on M(dmit)$_2$. Now is the time to start a full-scale study of them, for there remains much to be clarified about their electrical behavior and also still remain many related systems to be explored. The second subject of this thesis concerns a systematic elucidation of the electronic structures of M(dmit)$_2$ systems and further development of

them by synthesis of new ones with referring to the experimental information on the electronic structures.

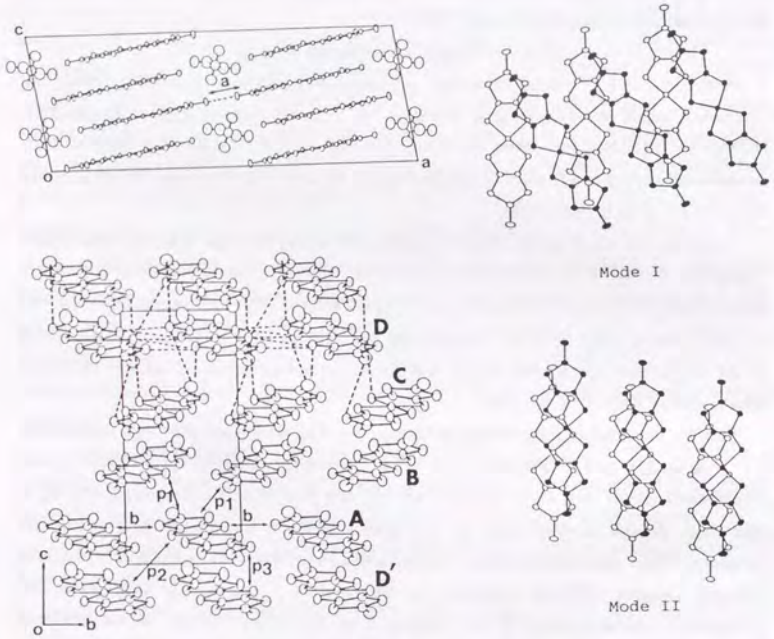
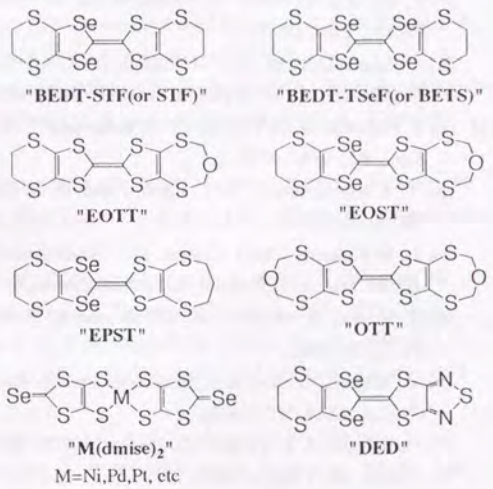


Figure 1.9. Crystal structure and molecular arrangement in α-$(CH_3)_2(C_2H_5)_2N[Ni(dmit)_2]_2$. Mode I and II denote the interdimer (*e.g.* C and D) and intradimer (*e.g.* B and C) overlapping modes, respectively. The Mode I is named spanning overlap.

1-4. Scope of This Thesis

In the course of the present study, the author has mainly concentrated on designing of new synthetic metals and superconductors by making the most of each unique property of BETS and its derivatives as well as $M(dmit)_2$ and $M(dmise)_2$ compounds. This is carried out by taking all the information available such as crystal and electronic structures and electrical behavior into consideration to discuss them. Chapter 2 deals with new organic conductors based on BETS salts, from various metals to a superconductor. The following Chapters 3 to 5 concern unsymmetrical donors derived from BETS. The synthesis, structures and electrical properties of the salts of a new donor BEDT-STF, which has the closest molecular resemblance to ET known to date, appear in Chapter 3 and are discussed in connection with the effect of disorder. The control of the dimensionality of intermolecular interaction, tried through synthesis of the salts of a new donor named EOST, is the subject of Chapter 4. In Chapter 5 the author attempted synthesis of novel donor salts, which would be interesting in magnetic and metallic properties at the same time, and are discussed from such a point of view. The last two chapters concern the study on the acceptor systems. $M(dmise)_2$, a relatively unexplored derivative of $M(dmit)_2$ has been synthesized and its new salts and complex were prepared, which are discussed in Chapter 6. Chapter 7 reports the electronic structures of a series of isostructural $M(dmit)_2$ salts determined by optical study.



Scheme 1.2. New molecular components of organic conductors developed in the course of this study and their related molecules.

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Chapter 2.

Synthesis, Crystal Structures and Electrical Properties of New Conducting Organic Salts of Bis(ethylenedithio)-tetraselenafulvalene (BETS)

2-1. Introduction

As reviewed in Chapter 1, the advancement of organic or molecular conductors accelerates by an emergence of a novel molecular system. But there remain many molecules of importance to be studied mostly due to the synthetic problems such that the synthesis is difficult and/or laborious, the molecule is insoluble and hard to purify or electrolyze, the single crystals of charge transfer salts are hardly obtainable, the resultant single crystals of the salts are not stable enough for further study and so on. In regard to donor systems the salts of BEDT-TSeF, or more simply BETS { = bis(ethylenedithio)tetraselenafulvalene }, are found among them. BETS was first reported by Schumaker *et al.* in 1983 [1] but the the properties of its cation radical salts had remained elusive for nearly ten years probably due to the synthetic difficulties until R. Kato *et al.* reported an improved method of the synthesis which avoids the use of highly toxic and malodorous reagents as CSe_2 and H_2Se [2]. This method offers the following advantages:

— moderate to high yields in all steps with sufficient reproducibility,
— reasonably good purity of crude products making purification easier if required,
— relatively short individual reaction times for a multi-step synthesis, and
— may be used with wide application in the synthesis of TXF (X = S, Se, Te) derivatives.

Such preparative improvement has facilitated a systematic study of BETS compounds to be sure, but the author has more affirmative reasons for being particularly interested in them.

— First, BETS is a closely related donor molecule to well-known ET but was expected to form a more isotropic and thus more stable molecular metal owing to its four selenium atoms introduced in the TTF skelton [2]. Through comparison of the results of BETS system with those of ET system, we could obtain information on the effect of the substitution of the selenium atoms for the sulfur atoms.

— Secondly, this similarity would give us another kind of chance; BETS might yield a series of superconductors.

— Thirdly, previous study showed BETS' strong tendency to form stable metallic salts with various anions [2]. In fact BETS has produced the largest fraction of metallic salts among yet reported donors [2 – 6]. In order to make the most of the BETS' features, the author selected the following kinds of salts to pursue.

Halogenomercury anions are very flexible and adapt themselves in the crystal to make salts with diverse cations, though often with disorder and/or solvent molecule and/or incommensurate sublattice [7 (a), (b), (d), 8, 9 (b), (c), (e), 10 (b)]. In the case of ET radical salts there have been reported ten kinds of bromomercurate salts [7 (a), 9], three kinds of chloromercurate salts [7 (b), 9 (b), 10] and three kinds of iodomercurate salts [9 (b), (d)]. Many of them exhibit some of the structural features indicated above; non-stoichiometry, solvent inclusion, different coordination numbers, various chemical situation such as bonded and non-bonded atoms surrounding mercury and thus total shape, size and net charge of the Hg complex anion. Accordingly their electrical properties are diverse. The author noted that some of them have turned out to be superconductors [7 (a), (b), 9 (b), (h), (i)] or at least have a similar donor arrangement with superconductors [9 (c), (d), (f), 10 (a), (b)]. Typical two-dimensional donor arrangements promising for stable metals and superconductors are the κ– and θ–type ones [11, 12]. The κ-type donor arrangement was originally discovered independently by two groups [11 (d), 12] and ever since almost every new κ-type ET salt renewed the record of T_c of organic superconductors [7] up to the one with the highest T_c [7 (f), (g)]. Although the least disorder is known to influence seriously the transport properties, such varieties in crystal structures would lead to a variety of new conducting salts. As a result new κ– and θ–type bromomercurate salts have been found by the present study [5], which are discussed in § 2-3.

The author also tried to synthesize the salts with such anions that did not yield metallic salts or even single crystals of sufficient quality with other donors. The MX_4^{n-} anions in particular (M = transition metals; X = halogens; n = 1,2) drew the author's attention. They are meant for the electronic system where π electrons from metallic band of the organic donor molecule interact with d electrons of comparatively localized level of the transition metal [13]. Yet in fact all but one [13 (d), (e)] are reported to be insulators and few cases have been reported to realize such system [6, 14]. Thanks to the advantageous nature to form stable metallic state when it forms a charge-transfer salt, BETS seems to be a hopeful donor to contribute to realize this important possibility. The tetrachloroferrate salt λ-$BETS_2FeCl_4$ illustrates this point [6, 3 (b)]; the realization of such system has been proved by the ESR and electrical resistivity measurements in § 2-4. Since the ground state of an analogous salt *without* a magnetic anion is intriguing as well, the author was encouraged to synthesize such salts, which has led to the finding of a new organic superconductor λ-$BETS_2GaCl_4$ [3], which is also described in this Chapter (§ 2-4).

2-2. Experimental

Materials

All chemicals are reagent grade from Wako Chemicals Co. and used as received unless noted otherwise. Triethyl phosphite was vacuum distilled, sealed under nitrogen and stored in the refrigerator until use. All solvents were degassed with high-purity dry nitrogen for at least a few minutes before use. All the materials were confirmed by elemental analyses or spectroscopic methods {IR, UV, NMR, MS(70 eV), GC} or some combination of them. BETS was synthesized following the literature procedure [2]. The supporting electrolytes are prepared as follows. Variations in the amount of solvents, scales did not influence considerably the yields in the following syntheses.

$[(C_4H_9)_4N]_2HgBr_4$, $[(C_4H_9)_4N]_2HgI_4$ and $(PPN)_2HgCl_4$

{PPN=bis(triphenylphosphoranylidene)ammonium, $[(C_6H_5)_3P=]_2N^+$} was prepared by treating the metal halide with the ammonium halides in ethanolic solution. The resulting precipitates were recrystallized from acetone, hot ethanol, CH_3CN/ether or CH_2Cl_2/ether at least twice. Colorless { $[(C_4H_9)_4N]_2HgBr_4$ and $(PPN)_2HgCl_4$ } or pale yellow { $[(C_4H_9)_4N]_2HgI_4$ } needles. 92 – 96 %.

$R_4N{\cdot}MX_4$ (R=CH_3, C_2H_5, C_4H_9; M=Fe, Al, Ga, In, Tl; X=Cl, Br, I) [15]

Anhydrous Lewis acid (MCl_3: from Soekawa Chemical Co., Ltd: net 1 – 5 g; cut the ampoule open in the dry-box) and an equivalent of the tetraalkylammonium halide were poured into the proper solvent (distilled CH_2Cl_2, absolute ethanol or thionyl chloride; $SOCl_2$ usually gave the better results) and stirred under nitrogen atmosphere at room or, if necessary for the dessolution, elevated temperature (~ reflux) for a few minutes to half an hour. An elongated heating or unnecessary higher temperatures decomposed the desired complex product, which darkened the reacting mixture. The transparent solution usually with a yellow or delicate brown tint was cooled in the refrigerator for a few hours to precipitate crystalline powder. Filtration under nitrogen atmosphere using standard Schlenk technique [16] and recrystallization from absolute ethanol yielded hygroscopic air-, light- and moisture-sensitive fine needles {$(C_4H_9)_4N{\cdot}AlCl_4$ (colorless), $(C_2H_5)_4N{\cdot}AlCl_4$ (colorless), $(C_4H_9)_4N{\cdot}GaCl_4$ (colorless), $(C_2H_5)_4N{\cdot}GaCl_4$ (colorless), $(CH_3)_4N{\cdot}GaCl_4$ (colorless), $(C_2H_5)_4N{\cdot}InCl_4$ (colorless), $(C_2H_5)_4N{\cdot}TlCl_4$ (colorless)}. A careful evaporation of the mother liquor to the fourth of its original volume under reduced pressure and exclusive of moisture gave second crop of enough purity. The yields were around 30 – 50 % depending on the cations and anions, the solvent used, how many times

recrystallized and how much evaporated. For a typical example, $(C_2H_5)_4N{\cdot}GaCl_4$ was synthesized as follows;

$(C_2H_5)_4N{\cdot}Cl$ (4.70 g) was dissolved in $SOCl_2$ (25 ml) and $GaCl_3$ (5.00 g) was added to the solution. The reacting solution was gently heated and evaporated to the fourth of its original volume under reduced pressure and cooled to - 40 °C. The colorless fine needles was filtered under nitrogen and washed with small amount of cold $SOCl_2$. The crude product was recrystallized from absolute ethanol.

$R_4N{\cdot}FeCl_4$ {$(C_4H_9)_4N{\cdot}FeCl_4$ (yellow), $(C_2H_5)_4N{\cdot}FeCl_4$ (yellow), $(CH_3)_4N{\cdot}FeCl_4$ (yellow)}was also prepared from $FeCl_3{\cdot}6H_2O$, the appropriate $R_4N{\cdot}Cl$ and ethanol instead of the reagents above.

$(C_4H_9)_4N{\cdot}FeBr_4$ was prepared by the direct reaction at -78 °C between $(C_4H_9)_4N{\cdot}FeCl_4$ and excess HBr/Br_2 mixture (dried over $CaSO_4$) evolved *in situ* from conc.H_2SO_4 and HBr aq.[17] for three hours and then gradually warmed to room tempearture under stream of nitrogen. The resultant reddish brown solid was recrystallized from ethanol to yield dark brown shiny needles.

For other $R_4N{\cdot}MBr_4$, {$(C_2H_5)_4N{\cdot}AlBr_4$ (pale orange or yellow), $(C_2H_5)_4N{\cdot}GaBr_4$ (colorless), $(C_2H_5)_4N{\cdot}InBr_4$ (colorless), $(C_2H_5)_4N{\cdot}TlBr_4$ (pale orange)} the identical procedures mentioned above were applied except for the reagents used; MBr_3, R_4NBr and distilled CH_2Cl_2 or thionyl bromide (the former solvent usually gave the better results); recrystallization from CH_2Br_2 or $SOBr_2$ was also possible though the latter solvent was not so stable at refluxing temperature.

For $R_4N{\cdot}MI_4$ {$(C_4H_9)_4N{\cdot}GaI_4$ (colorless), $(C_2H_5)_4N{\cdot}GaI_4$ (colorless), $(C_4H_9)_4N{\cdot}TlI_4$ (reddish orange)}, the similar procedures using MI_3, $R_4N{\cdot}I$ and CH_2Cl_2 were applied.

$R_4N{\cdot}MX_4$ (R=CH_3, C_2H_5, C_4H_9; M=Mn, Co, Ni, Cu, Zn; X=Cl, Br) [18]

They were synthesized by metathesis of equivalent amounts of $R_4N{\cdot}X$ and $MX_2{\cdot}nH_2O$ in absolute ethanol and recrystallized from hot ethanol several times and vacuum dried. The yields were around 60% depending on the cations and anions, the solvent used, how many times recrystallized and how much evaporated. They were generally shiny crystalline powder or fine needles; $(R_4N)_2MnX_4$ (pale yellow), $(R_4N)_2CoX_4$ (blue), $(R_4N)_2NiX_4$ (blue), $(R_4N)_2CuCl_4$ (orange), $(R_4N)_2CuBr_4$ (black), $(R_4N)_2ZnX_4$ (colorless).

Preparation of Single Crystals of the BETS Salts

The single crystals of the charge-transfer salts were obtained by electrocrystallization of BETS (7–10 mg) in the proper solvent (20 ml) with the supporting electrolyte(s) under nitrogen atmosphere at room temperature for one or two weeks. A cell without glass frit and platinum electrodes (1 mmϕ wires) were used unless otherwise noted. Usually the current was kept constant, but sometimes the voltage between the two electrodes was kept constant instead. The detail conditions of each case are tabulated in Tables 2.1 and 2.2.

Table 2.1. Electrolytic conditions of BETS[a]

counter ion[b] (X^{n-})	crystal habit[c]	current[d] /μA	voltage[e] /V	$(C_4H_9)_4NX$[b] /mg	BETS /mg	solvent[f]	time /days
$HgBr_4^{2-}$	(κ-)plates	0.6	—	154.2	8.0	TCE(Et)	4
$HgBr_2$	(θ-)plates	0.8	—	193	5.6	CB(Et)	2
TBA·Br				68			
18-crown-6				46			
KBr				108			
$HgBr_2$	(#2)plates	0.5	—	190	7	TCE(Et)	5
TBA·Br				86			
18-crown-6				77			
KBr				121			
$HgBr_2$	(#3)plates	0.6	—	115	9.0	CB(Et)	4
TBA·Br				103			
18-crown-6				168			
KBr				444			
HgI_4^{2-}		1.0	—	78	7	TCE(Et)	8
TBA·$FeCl_4$	(κ-)plates	1.0	—	37.2	12.4	CB	20
TMA·I	(λ-)needles			104			
$FeBr_4^-$	(κ-)plates needles	0.6	—	18.7	9.0	CB	30
TEA·$AlCl_4$	plates	1.0	—	33.1	6.7	CB	30
TEA·$GaCl_4$	(κ-)plates (λ-)needles	1.6	—	35.5	6.6	CB	5
TEA·$GaBr_4$	plates (λ-)needles	1.0	—	37.3	5.3	CB	24
TEA·$GaBr_4$	(κ-)plates needles	1.0	—	30.5	6.2	CB	24
TEA·GaI_4	plates (λ-)needles	2.0	—	30.5	3.3	CB(15ml)	70
TEA·$InCl_4$	(κ-)plates (#1)	1.0	—	30.5	6.0	CB(15ml)	10
TEA·$InCl_4$	plates (#2) needles (#3)	0.6	—	43.0	5.2	CB(Et 5%)	7
TEA·$InBr_4$	plates (λ-)needles	1.0	—	30.3	6.0	CB(Et 5%)	8
TEA·$TlCl_4$	(κ-)plates	1.0	—	29.1	7.2	CB	10
TEA·TlI_4	(κ-)plates	1.5	—	61.1	6.4	CB	2

Table 2.1. Electrolytic conditions of BETS (continued)[a]

[a] All syntheses were carried out at (20 ± 1) °C unless otherwise noted. [b] In case the supproting electrolytes were provided with combination of some reagents or other than tetrabutylammonium salts, the chemical formulae or abbreviations are indicated. TBA = tetrabutylammonium ion, 18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane. [c] All crystals are black. Plates are often elongated and appear needles at first sight. [d] Galvanostatic condition. [e] Potentiostatic condition. [f] 20 ml unless otherwise noted. TCE = 1,1,2-trichloroethane, CB = chlorobenzene, (Et) = the solvent containing 10 % ethanol (vol/vol) unless otherwise noted, THF = tetrahydrofuran.

Table 2.2. Detailed examination of electrolytic conditions of $(BETS)_2FeCl_4$[a]

	chlorobenzene	chlorobenzene + TMA·I	chlorobenzene (10 % ethanol)	otherwise
TBA	thin plates with much hairy stuff	robust plates and long, thick needles	plates and needles with few hairy stuff	chlorobenzene + TMA·I(35.3 °C)[b] large (5 × 5 mm^2)[c] thin plates and long (5 mm)[c] needles
TEA	slow growth, fairly large plates and needles	large plates and needles	plates and needles larger than those from CB alone	CB(1.7 °C)[d] thick plates
TMA	very slow growth, many fine platelets	—	very slow growth, fine platelets	

[a] Supporting electrolytes vs solvent(s), abbreviations in the Table: TMA·I = tetramethylammonium iodide, TBA = tetrabutylammonium tetrachloroferrate, TEA = tetraethylammonium tetrachloroferrate, TMA = tetramethylammonium tetrachloroferrate. [b] Done at 35.3 °C. [c] Average size. [d] Done in chlorobenzene (CB) at 1.7 °C.

Electrical Resistivity Measurements

All electrical resistivity measurements were carried out by a usual four probe method with dc current.

Over the range 4 – 293 K was measured by use of ^4He insertable cryostat and multi-channel 4-terminal conductometer (HUSO Electrochemical System, HECS 994)

controled by a personal computer (NEC PC-9801 Vm) through GPIB. Contact to the crystals was made by gold wires (15 μmϕ) attached with gold paste (Tokuriki Chemical, No. 8560) in the four-in-a-line configuration. The dc current was 0.1 μA.

Alternatively over the range 1.5 – 293 K a similar ^{4}He insertable cryostat was used. The dc current from 5 μA to 5 mA was supplied from Keithly 224 programmable current source. The current was dependent on the voltage between the two inner probe, which was monitored by Keithly 181 nanovoltmeter or Keithly 182 sensitive digital voltmeter. All procedures were controlled by a personal computer (NEC PC-9801 Vm) through GPIB.

Pressure dependence of the conductivity was measured using the same equipments mentioned above (those of the range 1 – 4 K) and a hydrostatic method employing a clump cell made of Cu/Be alloy (Toshiba Tangalloy) and Daphne oil (No.7373, Idemitsu Oil Co. Ltd.) as a pressure medium.

2-3. Structures and Electrical Properties of θ- and κ-Type BETS Salts with Bromomercurate Anions

There were four modifications in the crystals obtained. Let us number them from #1 to #4 for simplicity, distinguishing them by their conditions of the electrocrystallization. The solvent was either chlorobenzene (#1, #3) or 1,1,2-trichloroethane (#2, #4), both of which included 10% vol. of ethanol as shown in Table 2.1.

Phase #1: $(BETS)_4HgBr_4(C_6H_5Cl)_x$ ($x \approx 0.25$)

One of these phases (#1) was obtained as a black hexagonal platelet. The conductivity at room temperature was 10 $S \cdot cm^{-1}$. Anomalously small temperature dependence of the resistivity (Figure 2.1.) will not be an intrinsic nature of the system but possibly related to lattice defects, for this material contains disordered solvent molecules and the gradual loss of the luster of the crystal surface will be related to the loss of the crystal solvent. Such electrical behavior is reproducible on the different fresh samples but not old ones. Thus it may be concluded that this material is virtually metallic down to 4 K.

X-ray structural analysis gave the stoichiometry, BETS : $HgBr_4$: C_6H_5Cl = 4 : 4 : 0.25. The crystal data are as follows: θ-$(BETS)_4HgBr_4(C_6H_5Cl)_x$ ($x \approx 0.25$), tetragonal, $I4_1/a$, a = 9.742(1), c = 75.68(1) Å, V = 7182.5(2.1) Å^3. Figure 2.2 shows the crystal structure. BETS molecules form conducting layers normal to (001), while $HgBr_4^{2-}$ anions are located on the two-fold axes between the BETS layers. The Hg–Br

bond length is 2.59(1) Å and the bond angle of Br–Hg–Br is 109.5(2) °. To the author's knowledge, such a simple, discrete and hardly distorted tetrahedral bromomercury anion without disorder or incommensurate sublattice has not yet been reported as the counter anion in an organic metal. This is an important feature because they could scatter the conduction electrons at low temperature. Another feature is that this material contains a divalent anion, which has been considered to be disadvantageous in synthesis of conductive charge-transfer salts and actually is the first example in BETS salts and also rare in related salts, much less metallic ones. This will open up possibility of new organic metals and superconductors. The difference Fourier synthesis revealed the inclusion of the heavily disordered solvent molecules (C_6H_5Cl); the content of the solvent molecules included ($x \approx 0.25$) were roughly estimated from the occupancy probability of the Cl atom. Every BETS molecule is surrounded by other six BETS molecules. The dihedral angle between adjacent donor molecules (A and B in Figure 2.3) is 74 °. These structural characteristics indicate two dimensional electronic structure.

The extended Hückel tight-binding band calculation gave a two-dimensional (2D) Fermi surface, whose general trend is essentially the same as that of the organic superconductor θ-ET_2I_3 [11] (Figure 2.4). An organic conductor with a tetragonal unit cell, which means a perfect 2D crystal structure, is very rare, if not unprecedented [14 (a), (b), (k), 19]. This is an example illustrative of the trend of BETS salts that form close and isotropic intermolecular interaction based on the network of chalcogen-chalcogen short contacts. This salt clearly demonstrates the high potential or probability that BETS could realize a 2D stable metallic system in a charge-transfer salt when we choose a proper anion.

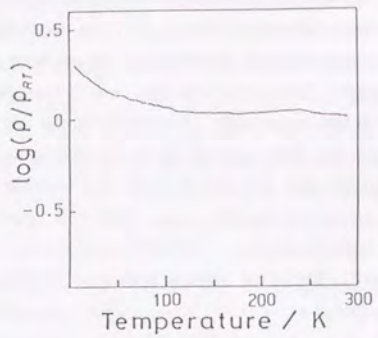


Figure 2.1. Electrical resistivity of θ−(BETS)4HgBr4(C6H5Cl)x

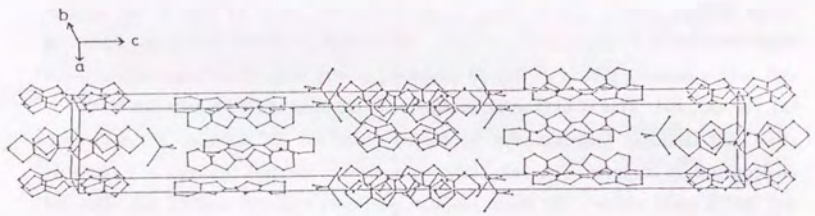


Figure 2.2. Crystal structure of θ−(BETS)4HgBr4(C6H5Cl)x The positions of C6H5Cl are omitted for clarity.

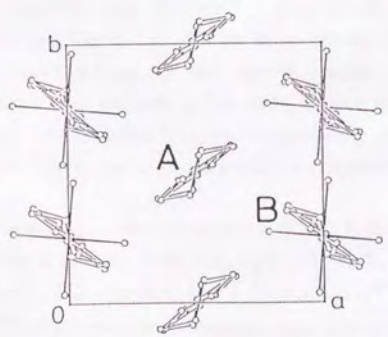
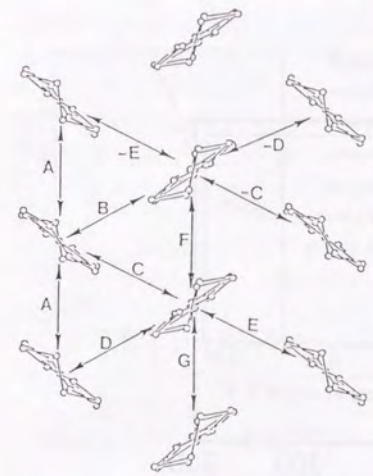
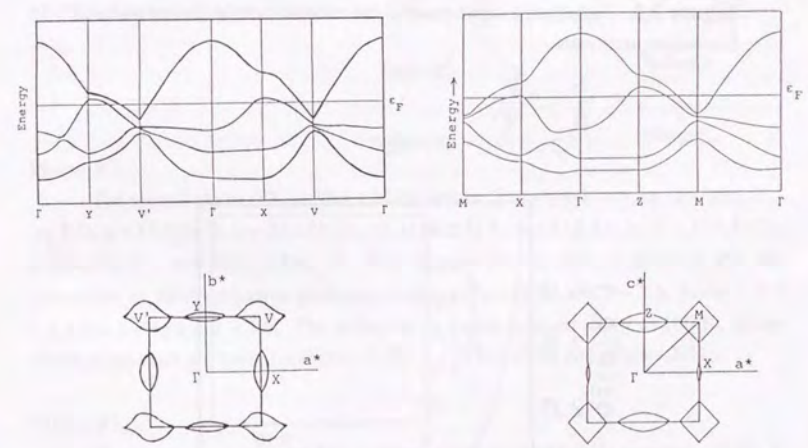


Figure 2.3. The molecular arrangement of BETS in θ−(BETS)4HgBr4(C6H5Cl)x



A	12.81	B	3.96
C	- 5.43	D	4.72
E	6.77	F	7.27
		G	5.67

(a)



(b) **(c)**

Figure 2.4. (a) Overlap integrals (× 10^3) of HOMO (highest occupied molecular orbital) calculated by extended Hückel method and (b) band electronic structure derived from tight-binding calculation in θ−(BETS)4HgBr4(C6H5Cl)x (x ≈ 0.25) along with (c) that of θ−(ET)2I3 [11] for comparison

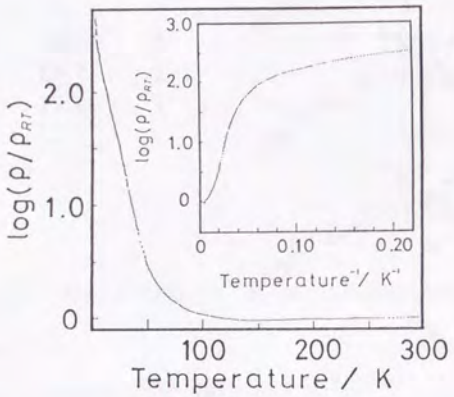


Figure 2.5. Temperature dependence of the resistivity of the second phase of bromomercurate salts

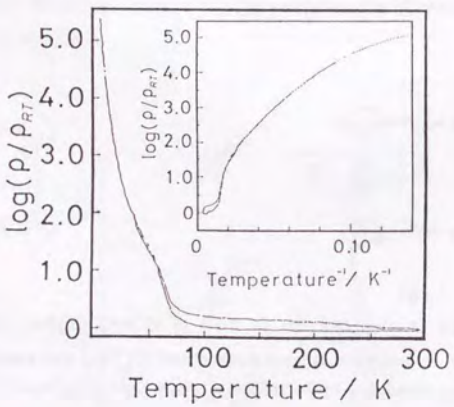


Figure 2.6. Temperature dependence of the resistivity of the third phase of bromomercurate salts

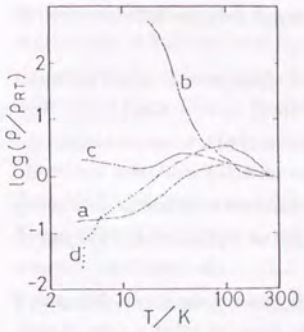


Figure 2.7. Sample dependence of the electrical resistivities of the crystals of monoclinic modification (κ-type) (a) A fresh sample (b) An old sample (c) After stored in the vapor of the proper solvent, the old sample recovered metallic property to some extent. (d) One fresh sample showing the resistivity drop around 5 K

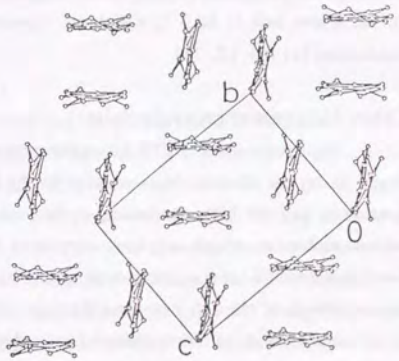


Figure 2.8. (Right-hand side) The κ-type molecular arrangement of BETS in the monoclinic modification

Phase #2

The second phase (#2) yielded a black needle. The crystal data are: triclinic, P $\bar{1}$ (or P1), a = 17.200(7), b = 22.331(7), c = 12.015(4) Å, α = 110.81(2), β = 110.51(3), γ = 64.01(3) °, V = 3772.0(2.6) $Å^3$. The ratios of the numbers of atoms in this salt determined by EPMA (electron probe micro analysis) are: S/Br = 2.5 – 3.5, Se/Br = 2.5 – 3.5 and Br/Hg = 4.0 – 5.5. The resistivity is almost constant down to 100 K, below which it increases gradually {ρ/Ω·cm ≈ 2 (RT – 100 K), 87 (4 K)} (Figure 2.5).

Phase #3

The third phase (#3) exhibits a sharp metal-insulator (MI) transition at 60 K (Figure 2.6). The poor quality of the crystal prevented the X-ray structural analysis. X-ray photograph gave strong diffuse scatterings.

Phase #4

The fourth phase (#4) was harvested as black platelets. Consecutive X-ray photographs demonstrated that the crystal gradually collapsed presumably by giving off the crystal solvent molecules. Therefore the behavior of the electrical resistivity strongly

depends upon the deterioration of the samples as shown in Figure 2.7. In one fresh sample, the resistivity seemed to drop around 5 K (d), though the same behavior was not reproduced.

The crystal belongs to the monoclinic system with space group C2/c and the lattice constants of a = 39.064(15), b = 8.654(4), c = 11.516(5) Å, β = 106.13(3) °, V = 3739.9(2.7) $Å^3$. The Br/Hg ratio (3.7 – 5.3) obtained from EPMA seems to suggest the existence of $HgBr_4^{2-}$ anion. Although the arrangement of BETS molecules was easily deduced and refined, the positions of Hg and Br atoms could not be determined definitely due to their heavy disorder. The mode of the arrangement of BETS molecules is that of the typical κ-type organic superconductors (Figure 2.8). The intradimer distance between BETS molecule is 3.50 Å and the dihedral angle between the dimers interrelated by the screw axis is 80.3 °, which are comparable to those of other κ-type organic conductors [11 (d), 12, 20].

Other Halogenomercurate Salts

The results about BETS bromomercurate salts mentioned above well reflect the expected crystal characteristics peculiar to the halogenomercurate ET salts. Generally speaking, they are high conducting to be sure, but poor crystal quality and included solvent molecules, which may have something to do with disorder, are disadvantageous for a stable metallic and superconducting state. In order to improve this point the author tried synthesis of chloro-, iodo- and thiocyano-mercurate BETS salts. The single crystals of an iodomercurate salt were obtained and exhibited metallic property down to *ca.* 90 K, at which temperature the resistivity turned to increase gradually (Figure 2.9). Since the resistivity at 4 K is not so high (less than 3 orders of magnitudes high) compared to the room temperature resistivity, the ground state of this material

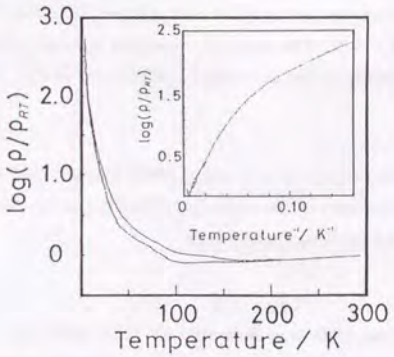


Figure 2.9. Temperature dependece of the resistivity of the iodomercurate salt

does not seem to be semiconducting. The X-ray photographs revealed that it might have the lattice constants of *ca.* 8.5 Å and 12.3 Å and belong to the monoclinic system, which suggests that it might be isostructural with the κ-type bromomercurate salt, and that it also has disorder in the crystal. The raise of the resistivity at low temperature might arise from a localization effect of the disorder.

2-4. Structures and Electrical Properties of κ- and λ-Type BETS Salts with Tetrahedral Anions

Crystal Structures and Electrical Properties of The FeX_4 (X = Cl, Br) Salts

κ– and λ–$(BETS)_2FeX_4$ (X = Cl, Br)

The X-ray structural analysis revealed that the plate crystals of $FeCl_4$ and $FeBr_4$ salts are isostructural (monoclinic, Pnma) to each other and, worth noting, to the organic superconductors with the highest T_c's, κ-$(ET)_2Cu[N(CN)_2]X$ (X = Cl, Br) [7 (f), (g)]. On the other hand the needle crystal of the $FeCl_4$ salt was found to belong to triclinic system with a novel donor arrangement. This new donor arrangement was named λ-type. The needle crystal of the $FeBr_4$ salt was semiconducting from room temperature and was not examined further. Their crystal data are listed in Table 2.3 along with those of some related salts, which will appear later in this section. As shown in Figure 2.10, the BETS molecules in λ-type structures are apparently aligned along [100] with fourfold quasi-stacking structure. However there are also found many chalcogen-chalcogen (Se---Se, Se---S and S---S) contacts shorter than the van der Waals distances (3.70, 3.85 and 4.00 Å, respectively) along [001] direction, which suggests the structure is 2D. The mode of the intermolecular overlapping between A and B in Figure 2.10 and that between A and A' are so-called ring-over-bond type, which is a common feature observed among superconducting κ-type salts [11(d), 12, 20]. However, between B and B', the central double bond does not sit on a five-membered ring, but instead on a six-membered ring. This may have something to do with the donor's structural peculiarity that one of the terminal ethylene groups is concave as if they yield some room, fringed by those of B, A and A', to the anion. The BETS molecule is normally planar in the salts as well as the cases with other similar donors. This structure does not suffer from any disorder at the ethylene groups or the anion nor includes solvent molecules, and is stable in the air. Judging from such stability and the good quality, rather large size and well-shaped form of the crystals, $FeCl_4$ anion seems to fit BETS very well to form salts. And what is more λ-$BETS_2FeCl_4$ exhibited metallic behavior down to 8 K. This is the second example of

the organic donor system with a magnetic anion that retains metallic property down to such low temperatures, preceded by $ET_3CuCl_4 \cdot H_2O$ [14 (i)]. The resistivity slightly increased on decreasing temperature and it made a maximum around 90 K. Below 90 K it decreased rapidly and at 8 K the material made a sudden transition into an insulator. This electrical behavior, a maximum around 90 – 100 K after which the resistivity decreases rapidly and occurs a sharp transition at *ca.* 8 – 10 K, keenly resembles that of κ-type superconducting salts except that the transition is that of metal-insulator (MI).

Meanwhile, as mentioned above, the plate crystals of $FeCl_4$ and $FeBr_4$ salts turned out to possess a κ-type structure; the crystal consists of the dimer of BETS molecules arranged in the characteristic orthogonal way (see Figure 2.11). They are the first examples to have κ-type donor arrangements with tetrahedral discrete anions; all previous examples have polymeric anions except for the first example of the superconductor of this class κ-ET_2I_3 [12 (b)], which contains linear anion. Similar to the case of the λ-type salt, the tetrahedral anions and the ethylene groups are all ordered. The electrical behavior of the $FeCl_4$ salt isdifferent from a typical κ-type behavior of the $FeBr_4$ salt (Figure 2.12). The room temperature conducivity of the $FeCl_4$ salt was about 50 $S \cdot cm^{-1}$ and monotonically reduced its resistivity down to 2 K. The residual resistance ratio ρ(300 K)/ρ(4 K) in the $FeCl_4$ salt is larger than 300, a surprisingly large value for a metal, still less an organic conductor with a magnetic anion.

Table 2.3. Crystal data of λ– and κ–$(BETS)_2MX_4$ [a]

	λ–$GaCl_4$	λ–$FeCl_4$	κ–$FeCl_4$	κ–$GaBr_4$	κ–$GaCl_4$
a/Å	16.141(3)	16.164(3)	11.663(8)	11.773(2)	11.665(5)
b/Å	18.580(3)	18.538(3)	35.856(12)	36.635(7)	35.894(9)
c/Å	6.594(1)	6.593(1)	8.456(4)	8.492(2)	8.464(3)
α/°	98.37(1)	98.40(1)			
β/°	96.77(1)	96.67(1)			
γ/°	112.55(1)	112.52(1)			
V/$Å^3$	1774.0(5)	1773.0(5)	3536(3)	3663(1)	3544(2)
S.G.	P $\bar{1}$	P $\bar{1}$	Pnma	Pnma	Pnma

Table 2.3. Crystal data of λ– and κ–$(BETS)_2MX_4$ (continued)[a]

	κ–$InCl_4$	κ–$FeBr_4$
a/Å	11.586(2)	11.754(5)
b/Å	36.492(2)	36.530(9)
c/Å	8.536(2)	8.482(2)
V/$Å^3$	3609(1)	3642(2)
S.G.	Pnma	Pnma

[a] In the course of this study, the structure of κ–$(BETS)_2GaCl_4$ has been coincidentally solved by Montgomery *et al.* independently [4 (c)].

Electronic Band Structures of λ-(BETS)$_2$FeCl$_4$

The tight-binding band calculation indicated that λ-(BETS)$_2$FeCl$_4$ has a 2D electronic structure which resembles those of κ-type salts (Figure 2.13). Although the donor arrangement is quite different from each other, the resemblance of the electronic structures is very interesting. Since κ-type ET salts produced the largest number of superconductors with higher T_c's (~ 10 K), the appearance of λ-type structure suggests a possibility of new series of organic superconductors with higher T_c could be found among the BETS salts of this class [2 – 4].

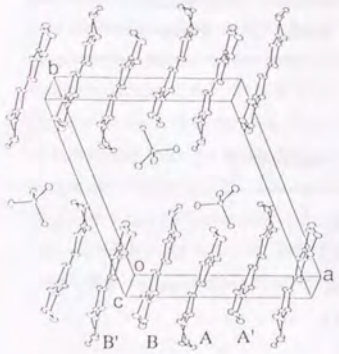


Figure 2.10. Crystal structure of λ-(BETS)$_2$FeCl$_4$

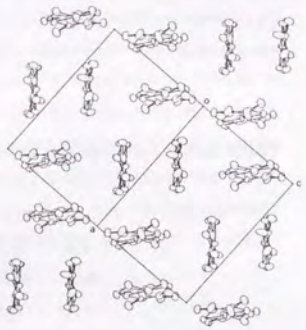
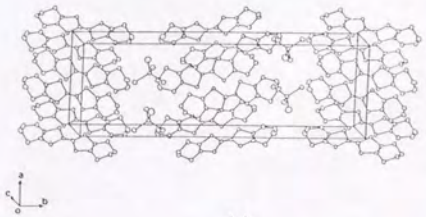


Figure 2.11. (a) Molecular arrangement in κ-(BETS)$_2$FeCl$_4$

(b)



(c)

Figure 2.11. (continued) (b) Intradimer overlapping mode and (c) crystal structure of κ-(BETS)$_2$FeCl$_4$.

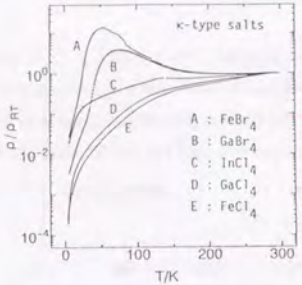


Figure 2.12. Temperature dependence of resistivities of κ-(BETS)$_2$MX$_4$

ESR Measurements

ESR measurements revealed that the magnetic property of λ-(BETS)$_2$FeCl$_4$ takes a transition at the same temperature (8 K; Figure 2.14) with that of the transition in the electrical behavior. This suggests that the magnetic anion Fe(III) plays an important role in the MI transition.

In regard to κ-(BETS)$_2$FeCl$_4$, ESR results did not indicate any magnetic transition down to the liquid helium temperature (Figure 2.15), nor a superconducting transition was confirmed down to 2 K. The ground state of this salt in itself as well as the contrast to the λ-type salt remains to be clarified.

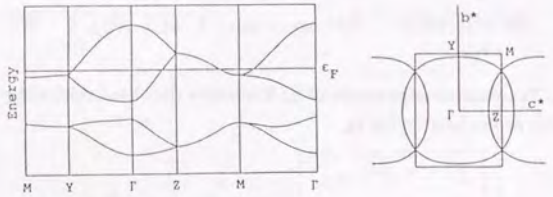


Figure 2.13. (a) Calculated electronic structure (left-hand side) and Fermi surface (right-hand side) of κ-(ET)$_2$I$_3$ (from ref.[11 (b)])

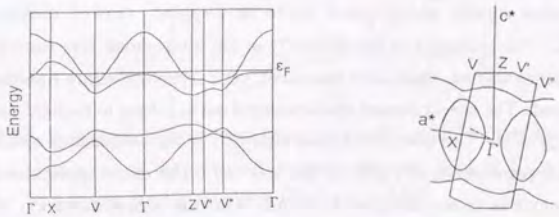


Figure 2.13. (continued) **(b)** Calculated electronic structure (left-hand side) and Fermi surface (right-hand side) of λ-(BETS)$_2$FeCl$_4$

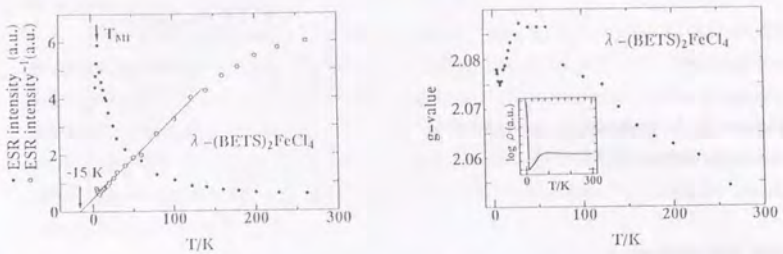


Figure 2.14. Temperature dependence of ESR intensity (left-hand side) and g-value (right-hand side) of λ-(BETS)2FeCl4

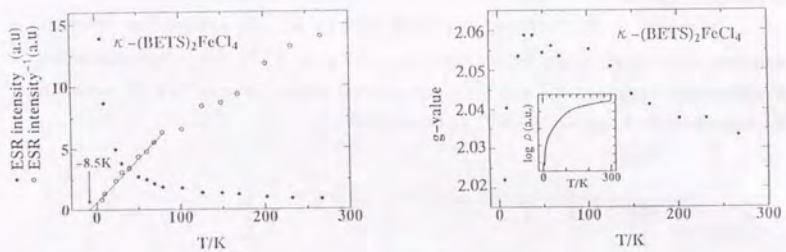


Figure 2.15. Temperature dependence of ESR intensity (left-hand side) and g-value (right-hand side) of κ-(BETS)2FeCl4

Crystal Structures and Electrical Properties of The Non-Magnetic MX_4^- Salts

The GaCl4 Salts

The plate crystal, which turned out to be κ-phase, showed metallic behavior down to 2 K. The reduction of the resistivity at low temperature was particularly steep and the resistance was too small to be measured, yet a superconducting transition has not been confirmed. The needle shaped crystals turned out to belong to triclinic, isostructural to λ-(BETS)2FeCl4. This compound leads electricity in the longitudinal direction of the crystal, which corresponds to *c*-axis of the unit cell. The donor molecules apparently stack along *a*-axis as shown in Figure 2.16 and *c*-axis runs almost along the side-by-side direction of them. This is very unusual for previous donor systems and is characteristic of λ-type salts, which demonstrates the strength of the in-plane intermolecular interactions between BETS molecules. It exhibited a temperature dependence of the

resistivity like a κ-type salt as show in Figure 2.17. From room temperature the resistivity slowly increased down to *ca.* 100 K, where it took a maximum and started to decrease rapidly to 8 K and then made a transition to a superconducting state, which was confirmed by a magnetic field. This is the first example of an organic superconductor based on BETS.†

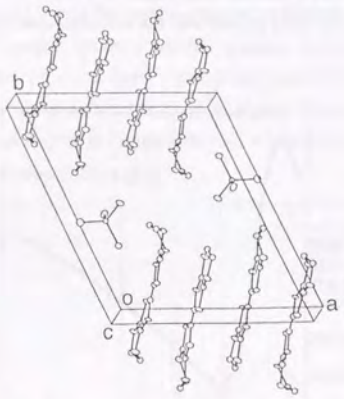


Figure 2.16. Crystal structure of λ-(BETS)2GaCl4

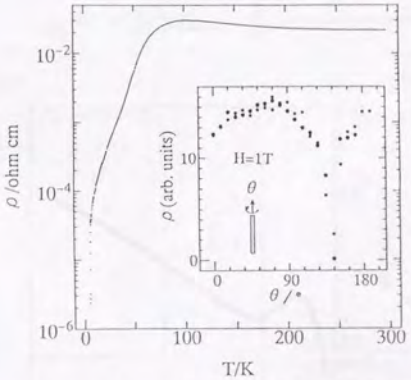
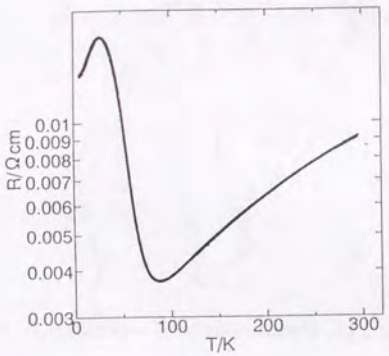


Figure 2.17. Temperature dependence of resistivity of λ-(BETS)2GaCl4 The inset is the angular dependence of the resistivity under a magnetic field (1 T) at 4.2 K. The direction of the magnetic field is parallel to (010) at θ = 145 °.

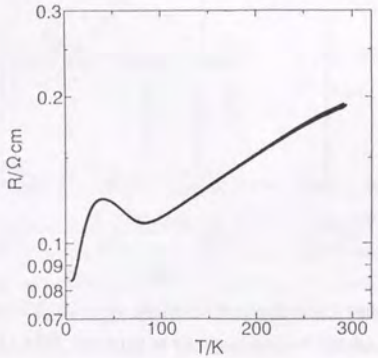
† In the course of the preparartion of this thesis, the second organic superconductor based on BETS λ-(BETS)2GaBrCl3 (T_c ~ 8 K) was found; H. Kobayashi, H. Tomita, T. Naito, H. Tanaka, A. Kobayashi and T. Saito, submitted to *J. Chem. Soc., Chem. Commun.*

The $AlCl_4$ Salt

The crystals were unstable in the air and the glisten of the surfaces rapidly turned dim and weak during the filtration. The Figures 2.18 (a), (b) show the electrical behavior measured immediately after the filtration (a) and the day after (b) on the same crystal. The old sample raised the resistivity twenty times as high as it had exhibited a day before, though qualitative behavior remained unchanged. Because of the vulnerability it shattered after the measurement; the same crystal was not obtained again and the crystal structure is unknown.



(a)

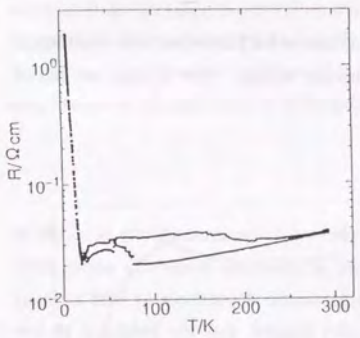


(b)

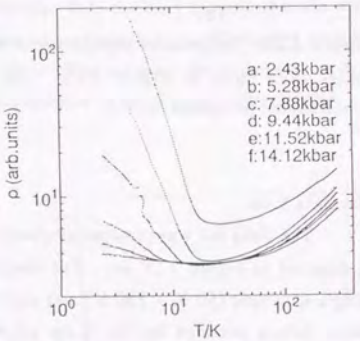
Figure 2.18. Temperature dependence of a plate crystal of BETS/$AlCl_4$ salt Behavior (a) immediately after the filtration and (b) the day after

The $GaBr_4$ Salts

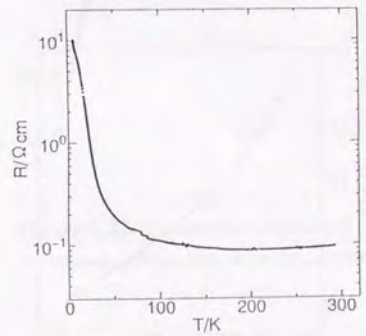
The $GaBr_4$ salt was obtained in four different crystal morphologies in total; two kinds of plates and two kinds of needles. The crystals (plates and needles) obtained by the first electrolysis behaved as shown in Figures 2.19 (a) to (d). They are both semiconductors at low temperature but the transitions were almost completely suppressed under higher pressure than 14 kbar. The plates (monoclinic) turned out to be different from κ-phase (see Table 2.3), while the needles belong to triclinic, λ-phase from the X-ray photographs. The crystals obtained by the second electrolysis have structures different from either of the previous ones. The plates have a κ-type structure, while needles included too many lattice defects for X-ray analysis. The former exhibited typical κ-type electrical behavior as shown in Figure 2.20 (b), while the latter is semiconductive from room temperature { Figure 2.20 (a)}.



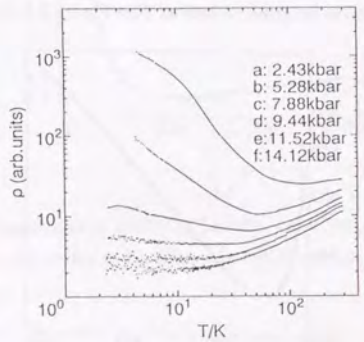
(a)



(b)

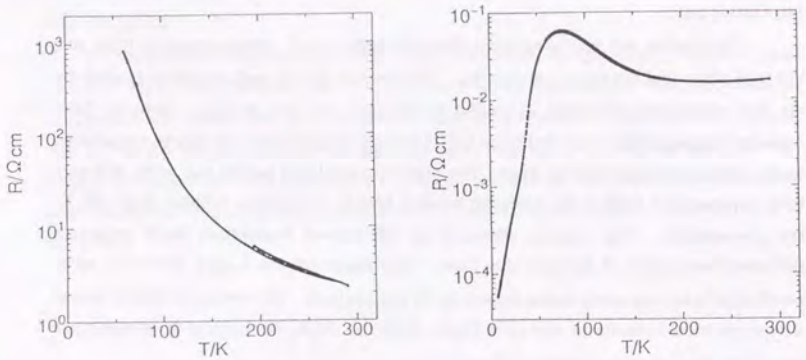


(c)



(d)

Figure 2.19. Temperature and pressure dependence of resistivities of BETS/$GaBr_4$ salts (a), (b) a plate crystal of monoclinic phase; (c), (d) a needle crystal of triclinic phase

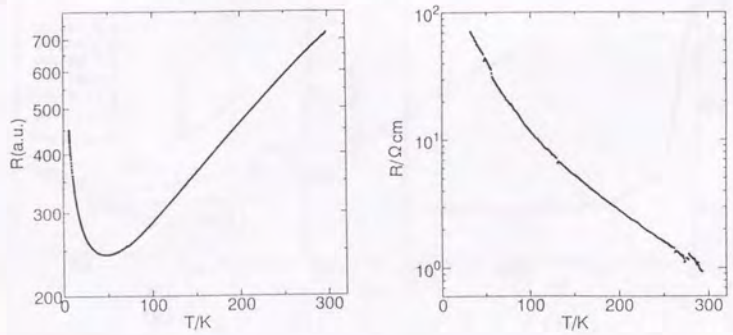


(a) (b)

Figure 2.20. Temperature dependence of resistivities of BETS/GaBr4 salts of different phases from those in Figure 2.15 (a) a needle crystal; (b) a plate crystal of orthorhombic (κ−)phase

The GaI4 Salts

The GaI4 salt was obtained as plates and showed minimum resistivity at *ca.* 50 K as depicted in Figure 2.21 (a). The temperature of minimum resisitivity varies from sample to sample (50 K – 150 K) and such a large sample dependence as well as many lattice defects revealed by the X-ray photographs suggest that the behavior at low temperature was not an intrinsic one. The needles turned out to belong to λ-type crystals and to be semiconductors {see Figure 2.21(b)}.

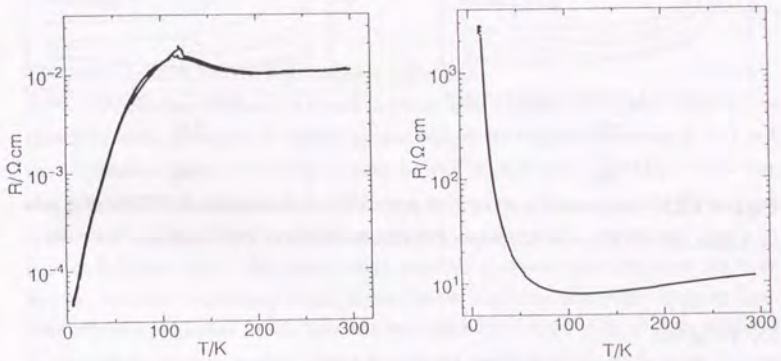


(a) (b)

Figure 2.21. Temperature dependence of resistivities of BETS/GaI4 salts (a) a plate crystal ; (b) a needle crystal of triclinic (λ−)phase

The InCl4 Salts

The plate crystal (#1) was turned out to have a κ−type crystal structure, whose electrical behavior is similar to that of κ-(BETS)$_2$GaBr$_4$ as shown in Figure 2.22 (a); they both show maxima in the resistivity around 100 K. κ-(BETS)$_2$InCl$_4$ has another anomaly in the resitivity at *ca.* 120 K, which was also observed in κ-(BETS)$_2$FeBr$_4$. They are reproducibly observed in every sample but the origin remains to be clarified. The plates (#2) and needles (#3) exhibited identical electrical properties {Figure 2.22 (b)}, which is different from the previous one. The X-ray analysis demonstrated that they (#2, #3) have the same structure. The unit cell could be rather complicated, judging from the crystal data; monoclinic, $P2_1/a$, a = 20.4695(4), b = 9.6703(12), c = 23.4438(18) Å, β = 96.638(11) °, V = 4609.50(1.19) Å^3. In many cases the chalcogen donor salts have a unit cell volume of a near multiple of 850 Å^3, but the volume of this compound deviates significantly from this tendency. This can have something to do with the fact that chloride complex anions of indium have reported to be able to take various shapes and coordination numbers [15 (a), (b)]. The raise in the resistivity at low temperature of this salt could be attributable to a disorder or some other lattice defects.

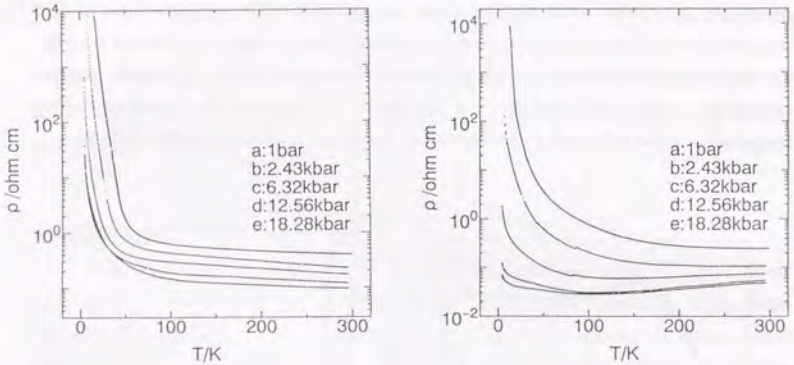


(a) (b)

Figure 2.22. Temperature dependence of resistivities of BETS/InCl4 salts. (a) a plate (κ−)crystal ; (b) another behavior common to the crystals (#2, #3) of the triclinic phase

The InBr4 Salts

The plate crystals showed narrowly metallic behavior around room temperature and made a smooth transition into an insulator below *ca.* 70 K even under 18 kbar as depicted in Figure 2.23 (a). The needle crystal is considered to be λ-type based on X-ray photographs and showed a qualitatively similar behavior to the former {see Figure 2.23(b)}. But the insulating phase of the λ-phase crystal was suppressed easily by pressuring and a clear metallic phase appeared under 12 kbar or higher pressure.



(a) (b)

Figure 2.23. Temperature and pressure dependence of resistivities of BETS/InBr4 salts (a) a plate crystal of monoclinic phase; (b) a needle crystal of triclinic phase

The TlCl4 Salt

The X-ray photographs indicated that this salt belongs to triclinic and that it has a κ-type structure. But most of the crystals were too fragile to measure the temperature dependence of resistivity. A preliminary measurement indicated that one sample behaved as other κ-type salts; it diminished the resisitivity slowly at room temperature but below *ca.* 180 K it slightly increased it to *ca.* 100 K, where it took a maximum, and then rapidly decreased it down to 4 K.

The TlI4 Salt

This was found to be insulators and not examined further.

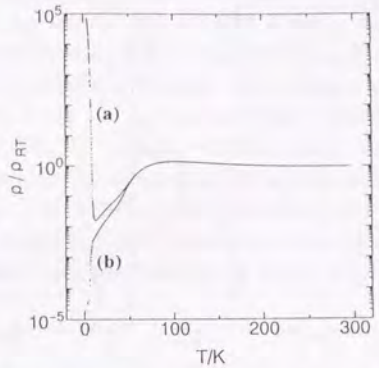


Figure 2.24. Temperature dependence of resistivities of λ-(BETS)2MCl4 (a) M = Fe, (b) M = Ga

The Alloy System λ-(BETS)2(GaCl4)1-x(FeCl4)x

The similarity between the two λ-phase salts (Figure 2.24) may offer a rare chance to study an organic π metallic system with dilute magnetic moments in it if one can synthesize a series of the alloy systems λ-(BETS)2(GaCl4)1-x(FeCl4)x, which may also give some information about their own properties. Some of such alloys were synthesized and their electrical behavior measured on the single crystals are shown in Figures 2.25 (a) – (d). Their actual stoichiometries or crystal structures have yet to be known, but these preliminary results already show interesting diversity. Judging from their behavior and crystal habits, they may be regarded as λ-type. One of them exhibited superconducting transition after a little upturn of the resitivity {(a)}, while some showed broad MI transitions {(b) and (d)}. The latter examples will provide us experimental information about the mechanism of the MI transition of λ-(BETS)2FeCl4 and origin of the contrast to the related κ-type salts. In connection with the result shown in Figure 2.21, an additional interesting and unusual behavior was observed in other alloy crystals as well as in pure λ-(BETS)2FeCl4 under high pressure or high magnetic fields [3 (b), 6 (b), (c)]; in total they suggest that superconductivity, insulating state driven by magnetic transition of the anion and/or disorder correlate each other. The research concerning to these results are so expansible that relevant study is now developing by several collaborator groups and promising for further intriguing discoveries.

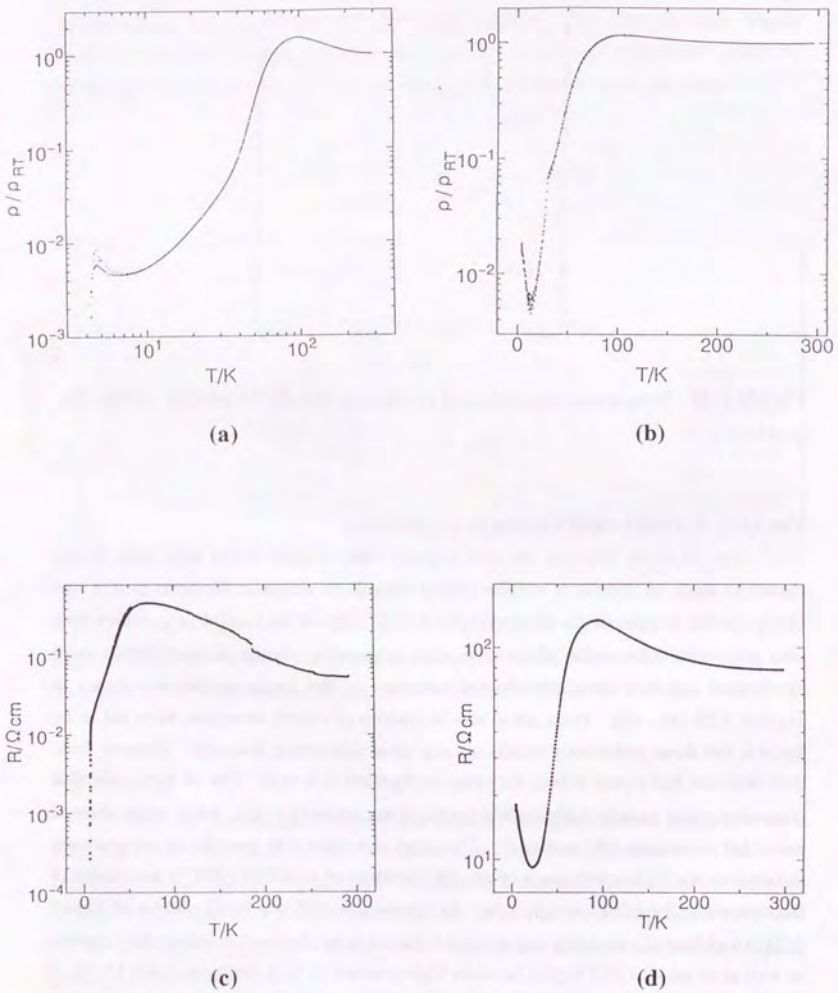


Figure 2.25. Temperature dependence of resistivities of the alloy system $(BETS)_2(GaCl_4)_{1-x}(FeCl_4)_x$ with various x and potentially λ-type structure. The mixing ratios of the supporting electrolytes in the electrolytic preparation, *i.e.* $(TEA{\cdot}GaCl_4)$: $(TEA{\cdot}FeCl_4)$, are (a), (b) 1 : 1, (c), (d) 10 : 1, respectively.

2-5. Summary

The charge-transfer salts of BETS with metal-halogen complex anions were newly synthesized and their crystal structures and electrical properties were examined. BETS has known to share many properties with ET in itself or charge-transfer salts, to be sure, but its unique ability to form stable 2D electronic structure with appropriate anions has been confirmed and extended by this study. For example, it is illustrated by the salts with such flexible anions as halogenomercurates; several new salts as θ-$(BETS)_4HgBr_4(C_6H_5Cl)_x$ ($x \approx 0.25$) exhibited crystal structures and electrical properties both similar to and different from any ET halogenomercurate salts. As for the IIIA-tetrahalide anion salts, λ-$(BETS)_2GaCl_4$ has been found to be a new organic superconductor with a rather high T_c of 8 K and with a novel donor arrangement, while λ-$(BETS)_2FeCl_4$ opened up a new possibility of organic donor system with magnetic moments.

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Chapter 3.

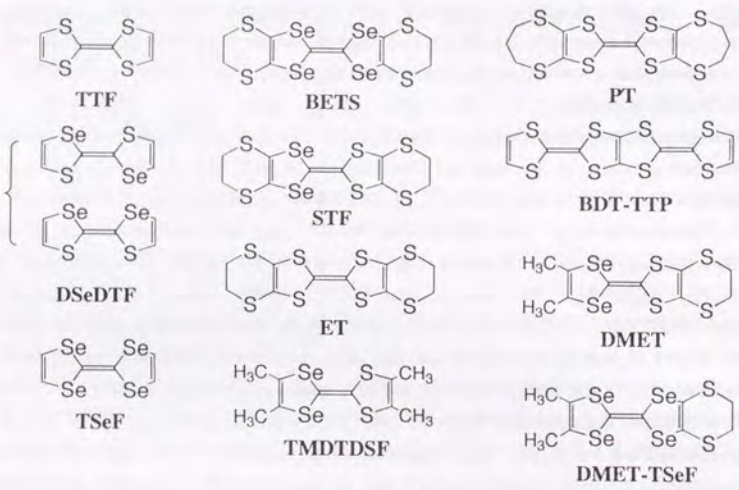
Synthesis of Charge-transfer Salts Based on New Unsymmetrical Donor Bis(ethylenedithio)-diselenadithiafulvalene (STF): Disorder Effect on Transport Properties

3-1. Introduction

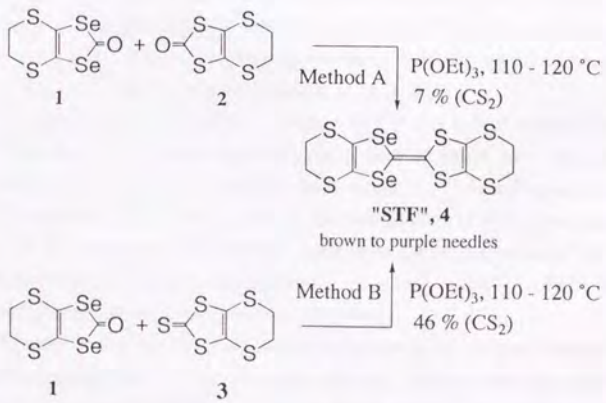
The research of chemistry and physics of organic superconductors have made a rapid progress in these years [1]. The major part of the accumulated data consists of those of BEDT-TTF { bis(ethylenedithio)tetrathiafulvalene, "ET" } system from all over the world mainly because this donor has proven to be a versatile building block for the design of an organic superconductor, sometimes with a higher transition temperature (T_c) than 10 K [2]. Indeed much of the current work in this field is aimed at increasing the T_c's. But no definitive guideline exists, to date, for predicting those material systems that will exhibit high T_c or novel superconducting mechanisms. In this respect, an empirical search for new materials remains the most effective approach. There have been some ways; some researchers, particularly physists, have investigated the transport or other properties of the ET salts to understand the superconducting mechanisms, and others such as chemists have devoted themselves to synthesis of similar systems based on close molecules. For example, some studies concerning the effect of defects in crystals on electrical properties [3] have originated from the former, whereas the latter have led to the advent of a variety of analogous donor molecules including unsymmetrical ones and their cation radical salts or complexes [1, 4, 5, 6].

The title donor (BEDT-STF or simply STF) is a hybrid molecule of ET and BETS { bis(ethylenedithio)tetraselenafulvalene }, both of which have been reported to yield a number of charge-transfer salts of stable metals [1, 7] including superconductors [1, 2, 8]. Therefore one of the impetus for the investigation of STF salts comes from a prospect of discovery of a new organic superconductor as demonstrated by DMET (dimethylethylenedithiodiselenadithiafulvalene) [4] and DMET-TSeF (dimethylethylenedithiotetraselenafulvalene) [6] salts.

Another motive for this study lies in an interest in the relation between disorder and electrical properties. There are some previous studies concernig the effects of disorder on the transport properties of organic donor systems using alloy samples or X-ray, proton or neutron irradiated samples or theoretical approach [3 (a) – (j), 9 (b), (e), (h), 10, 11], but the net effect of disorder was difficult to discuss, for there were some other lattice defects like impurities or inhomogeniety from alloying or due to the fact that disorder lay in the anion site instead of directly in the electrical path. In the present system the randomness can be introduced in the conduction layer without other perturbation. The STF salts will provide an unique approach for the systematic study of the metallic and superconducting properties of ET (, and probably also those of BETS) salts. In the meantime, compared with symmetrical donor salts, numerous unsymmetrical donor salts reported to date have no unique properties that result directly from the lower symmetry of the donor molecules except for the cases of DSeDTF (diselenadithiafulvalene) [9 (b), (e), (h)] and TMDTDSF (tetramethyldithiadiselenafulvalene) [10] salts, both of which are typical one-dimensional electronic systems. A structural and chemical keen resemblance between the two parts inherited from their parent donors (ET and BETS) distinguishes STF from other unsymmetrical donors. Such characteristic would cause orientational disorder of the donor packing in the solid state. If it happens, how does the metallic or superconducting property differ from the corresponding ET or BETS salts? Among organic superconductors, κ-$(ET)_2Cu[N(CN)_2]Br$ is one of the most interesting ones due to its the second highest T_c reported to date [2 (b)]. In order to contribute to the better understanding of the superconductivity in the κ-type organic charge transfer salts [11], the temperature dependence of T_c on the ratio (x) in κ-$[(ET)_{1-x}(STF)_x]_2Cu[N(CN)_2]Br$ is examined in § 3-4 [3 (k)]. This chapter report the synthesis of STF salts and discuss them with data of the crystal structures and electrical properties from the view point mentioned above.



Scheme 3.1.



Scheme 3.2.

3-2. Experimental

All chemicals were reagent grade from Wako Chemical Co. and used as received unless noted otherwise. Triethyl phosphite was vacuum distilled, sealed under nitrogen and stored in the refrigerator until use. All solvents were degassed with high purity dry nitrogen for at least a few minutes before use. 4,5-ethylenedithio-1,3-diselenole-2-one **1** [7 (a)], 4,5-ethylenedithio-1,3-dithiole-2-one **2** [12] and 4,5-ethylenedithio-1,3-dithiole-2-thione **3** [12] were prepared by following the reported procedure.

Materials

bis(ethylenedithio)diselenadithiafulvalene, **4**

Method A. The intermediates **1** (0.483 g, 1.6 mmol) and **2** (0.333 g, 1.6 mmol) suspended in triethyl phosphite (100 ml) were slowly heated with stirring to clear solution under nitrogen atmosphere. Succesive heating to 110 - 120 °C turned the solution from yellow to scarlet within a few minutes and precipitation occurred. The mixture was held in that temperature range with stirring for 30 min. After cooling to room temperature, reddish-brown precipitates were filtered off, washed successively with acetone, methanol, ethanol and hexane and dried *in vacuo*. The crude products were recrystallized from hot CS_2 (250 ml × 3) followed by column chromatography (silica gel, eluent CS_2), then HPLC (Kusano Kagaku-kikai Co., Si-10; eluent CS_2) gave analytically pure violet gemlike needles; yield: 50 mg (7 %). Elemental analysis: $C_{10}H_8S_6Se_2$ calculated(%) C: 25.10 H: 1.69 S: 40.21 Se: 33.00 ; found (%) C: 25.13 H: 1.76 S: 39.86 Se: 32.25. MS (EI, 70 eV): m/e = 480 (M+2: 100 %), 478 (M^+: 83 %). IR (KBr): 1407.8 (s), 1282.4 (s), 918.9 (s), 716.4 (s) cm^{-1}. For the crystal data, see Table 3.2 (later).

Method B. A similar procedure to method A was followed with **3** (0.359 g, 1.6 mmol) instead of **2**. This allowed highly selective reaction and only a trace amount of self-coupling products formed, which saved tedious work-up for isolation of the desired compound in method A; crude coupling products were filtered off from the phosphite, washed thoroughly with methanol, dried *in vacuo* and passed through short column (silica gel, eluent CS_2), then recrystallized from hot CS_2 once or twice; yield: 350 mg (46 %).

Charge-transfer Salts of STF

Single crystals of the charge-transfer salts of STF were prepared by use of standard electrocrystallization techniques. All chemicals were purified prior to use and handled inside a drybox. The crystal growth was carried out in a standard H-cell (

without glass-frit) using platinum electrodes of 1 mm in diameter under a nitrogen atmosphere. A typical procedure began with 7-12 mg of STF and 40 - 100 mg of the tetrabutylammonium salt of the desired anion as the supporting electrolyte in 20 ml of an appropriate solvent at a constant current at room temperature (19 - 21 °C) for several days. Sometimes potentiostatic condition, higher (lower) temperature and/or some other minor modification were applied. Actual each condition is tabulated in Table 3.1.

Table 3.1. Electrolytic conditions for preparation of STF salts [a]

counter ion[b] (X^{n-})	crystal habit[c]	current[d] /μA	voltage[e] /V	$(C_4H_9)_4NX$ /mg	STF	solvent[f] /mg	time /days
PF_6^-	needles	1.2	—	38	8	CB	9
AsF_6^-	needles	1.5	—	99	8	CB	9
SbF_6^-	plates	0.5	—	90	10	CB	4
TaF_6^-	needles	2.2	—	99	7	CB(Et)	9
BF_4^-	plates	—	5.4	65	10	CB(31 °C)	4
ClO_4^-	plates needles	0.3	—	120	7	CB/THF	4
ReO_4^-	plates(#1) needles(#2)	—	3.2	56	9	CB(31 °C)	7
ReO_4^-	plates(#3)	0.1	—	69	7	CB/THF	13
I_3^-	(α-)plates	—	1.0	101	12	CB(43 °C)	10
I_3^-	(α-)plates	—	12.0	30	7	CB(43 °C)	9
$AuCl_2^-$	plates	0.3	—	37	7	CB/THF	10
$AuBr_2^-$	plates	0.1	—	72	6	CB/THF[g]	9
AuI_2^-	plates(#1)	1.0	—	88	11	CB	18
AuI_2^-	plates(#2)	1.2	—	39	8	CB/THF[g]	7
AuI_2^-	plates(#2)	1.2	—	44	7	CB(Et)	7
$Au(CN)_2^-$	plates	0.3	—	56	7	CB/THF	10
$Ag(CN)_2^-$	plates	0.3	—	75	8	CB/THF	16
$HgBr_4^{2-}$	needles	0.2	—	109	8	CB/THF	7
TEA·$GaCl_4$	(κ-)plates (λ-)needles	1.3	—	60	10	CB(16 °C)	7
TEA·$FeCl_4$	plates needles	0.1	—	41	8	CB(16 °C)	8
$FeBr_4^-$	plates needles	0.6 0.3	— —	44 32	11 6	CB(16 °C) CB(16 °C)	4 4
TEA·$GaBr_4$	plates needles	0.1	—	54	8	CB(Et 5 %)	5
TEA·$InCl_4$	needles	1.2	—	42	7	CB(Et 5 %)	16
TEA·$InBr_4$	plates needles	1.0	—	44	7	CB(Et 5%)	16

Table 3.1. Electrolytic conditions of STF (continued) [a]

counter ion[b] (X^{n-})	crystal habit[c]	current[d] /μA	voltage[e] /V	$(C_4H_9)_4NX$ /mg	BETS /mg	solvent[f]	time /days
TEA·$TlCl_4$	needles	1.1	—	52	8	CB(Et 5 %)	16
TEA·$TlBr_4$	needles	1.2	—	54	7	CB(Et 5 %)	10
KNO_3	plates	1.4	—	30	8	THF	5
18-crown-6							33

[a] All syntheses were carried out at (20 ± 1) °C unless otherwise noted. [b] In case the supproting electrolytes were provided with combination of some reagents or other than tetrabutylammonium salts, the chemical formulae or abbreviations are indicated. TBA = tetrabutylammonium ion, 18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane. [c] All crystals are black. Plates are often elongated and appear needles at first sight.
[d] Galvanostatic condition. [e] Potentiostatic condition. [f] 20 ml unless otherwise noted. TCE = 1,1,2-trichloroethane, CB = chlorobenzene, (Et) = the solvent containing 10 % ethanol (vol/vol) unless otherwise noted, THF = tetrahydrofuran, CB/THF = 1:1 (vol/vol) mixture of chlorobenzene and tetrahydrofuran otherwise noted. [g] CB/THF = 9 : 1 (vol/vol) mixture of chlorobenzene and tetrahydrofuran.

Preparation and Characterization of Organic Alloy System; κ-[(ET)$_{1-x}$(STF)$_x$]$_2$Cu[N(CN)$_2$]Br

ET was synthesized following the reported procedure [12]. Single crystals of the alloy system were prepared electrochemically as described above. The two donors were measured and well mixed using agate mortar and pestle in an appropriate ratio inside a drybox. Actual each condition is tabulated in Table 3.3. The average size of the crystal used in the resistivity measurement was approximately 0.5 × 0.5 × 0.2 mm^3. The electrical conductivity of each single crystal was measured by usual dc four-probe method. After conductivity measurements, five (#1 – #5) crystals were submitted to X-ray crystal structure analyses. The stoichiometry (x-value) was determined by the refinement of the occupancy probability of Se (or S) in the TTF skeleton.

3-3. Synthesis and Solid State Properties of STF Salts with Various Anions

Synthesis of New Unsymmetrical Donor: STF

The new unsymmetrical donor was synthesized by two routes. Method A involves the two ketones to be coupled, whereas method B involves the 1,3-diselenole-2-one and the 1,3-dithiole-2-thione in the same reaction as method A. The cross-coupling of a 1,3-diselenole-2-one or -thione and a 1,3-dithiole-2-thione has been often reported to result in unexpected failure due to side reactions or rearrangement [9]. Another drawback to this procedure is that in many cases all possible coupling products are produced and they must be separated, which is sometimes very difficult [9 (c)]. However phosphorous base coupling is currently the only effective means of coupling the selenium analogues of TTF [13]. Although this coupling method has been known for more than 20 years, it still remains difficult to expect which derivatives among ketone, thione or selone should be used for the best yield in a particular case [14 – 18]. Krief concluded in his review that the mechanism of these reactions has not yet been elucidated and that it is very probable that it varies as a function of the heteroatom and the substituents on the heterocycle [13 (c)]. In this case both route (methods A and B) did not suffer from any rearrangement. The yield via method A was much lower than the other and the method required separation of three coupling products. It was accomplished mainly by HPLC using fine mesh Si gel (10 μm) and CS_2 as eluent. On the contrary method B produced the desired cross-coupling product with an unusually high yield and selectivity for cross-coupling reactions of this kind.

Synthesis of STF Salts by Electrochemical Method

As expected, the new donor molecule has turned out to have a closely related molecular structure as well as crystal structure to the all sulfur analogue, ET, but the electrolytic conditions for preparation of charge transfer salts and results of them often rather differ from what was extrapolated from those of ET. The charge-transfer salts of this donor have been prepared mostly in chlorobenzene. Other solvents such as dichloromethane, 1,2-dichloroethane or benzonitrile, which are all popular in electrolyses of ET, did not give a crystalline solid.

Table 3.2. Crystal data of STF, its charge transfer salts and related isostructural compounds

	ET[a]	STF	BETS[b]
	monoclinic	monoclinic	monoclinic
	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	6.614(11)	6.644(3)	6.662
b/Å	13.985(2)	14.148(4)	14.227
c/Å	16.646(3)	16.998(7)	16.216
β/°	109.55(2)	109.67(3)	92.97
V/Å^3	1449.6	1504.6	1534.9
Z	4	4	4

Table 3.2. Crystal data of STF, its charge transfer salts and related isostructural compounds (continued)

	α-$(ET)_2I_3$[c]	α-$(STF)_2I_3$	α-$(BETS)_2I_3$[b]
	triclinic	triclinic	triclinic
	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	9.211(2)	9.198(2)	9.209
b/Å	10.850(4)	10.802(3)	10.816
c/Å	17.488(5)	17.607(5)	17.777
α/°	96.95(2)	96.86(2)	96.63
β/°	97.97(2)	97.88(2)	97.87
γ/°	90.75(2)	90.75(2)	90.69
V/Å^3	1717	1719.7	
Z	2	2	2

Table 3.2. Crystal data of STF, its charge transfer salts and related isostructural compounds (continued)

	$(ET)_3(ClO_4)_2$[d]	$(STF)_3(ClO_4)_2$	$(STF)_2AuCl_2$	θ-$(STF)_2AuI_2$[e]
	triclinic	triclinic	monoclinic	orthorhombic
	$P\bar{1}$	$P\bar{1}$	P2/c	
a/Å	16.463(2)	16.702(6)	16.371(4)	34.094(24)
b/Å	9.498(2)	9.522(3)	6.718(1)	20.268(19)
c/Å	7.613(2)	7.634(2)	15.395(4)	9.928(9)
α/°	95.91(2)	95.65(3)		
β/°	87.17(1)	87.17(3)	105.72(2)	
γ/°	90.84(1)	91.16(3)		
V/Å^3	1182	1206.6	1629.8(6)	6860
Z	1	1	2	8

Table 3.2. Crystal data of STF, its charge transfer salts and related isostructural compounds (continued)

	λ-$(STF)_2GaCl_4$	λ-$(BETS)_2GaCl_4$[f]	κ-$(STF)_2GaCl_4$	κ-$(BETS)_2GaCl_4$[f]
	triclinic	triclinic	orthorhombic	orthorhombic
	$P\bar{1}$	$P\bar{1}$	Pnma	Pnma
a/Å	16.244(48)	16.141(3)	11.588(61)	11.665(5)
b/Å	18.355(43)	18.580(3)	35.696(20)	35.894(9)
c/Å	6.581(111)	6.594(1)	8.493(84)	8.464(3)
α/°	98.46(21)	98.37(1)		
β/°	96.90(19)	96.77(1)		
γ/°	112.46(41)	112.55(1)		
V/Å^3	1759.9	1774.0(5)	3512.8	3544(2)
Z	2	2	4	4

[a] From ref. [21] [b] From ref. [7 (a)] Neither cell volume nor standard deviations are not available in the reference. [c] From ref. [25] [d] From ref. [19] [e] Metallic phase (#1) X-ray structural analysis was not completed due to the poor quality of the crystal. [f] From ref. [7 (b)]

Table 3.3. Electrolytic conditions for preparation of κ-[(ET)$_{1-x}$(STF)$_x$]$_2$Cu[N(CN)$_2$]Br [a]

T_c / K	ET / mg	STF / mg	$CuBr_2^-$ / mg[b]	$N(CN)_2^-$ / mg[c]	Temp. / °C	results[d]
11.6 (#1)	8	0	43	37	24	0.1 × 0.1 mm^2
9.2 (#2)	6	2	32	30	19	0.8 × 1.0 mm^2
6.4 (#3)	9	4	44	55	19	0.7 × 0.3 mm^2
4.2 (#4)	6	6	52	37	20	1.0 × 1.0 mm^2
< 1.5 (#5)	1	5	38	36	19	0.1 × 0.2 mm^2

[a] All syntheses were carried out in the mixed solvents (20 ml) of 1,1,2-trichloroethane : ethanol : chlorobenzene = 9 : 1 : 10 under a galvanostatic condition (0.8 μA) for a week or two. [b] Provided as TBA·$CuBr_2$, where TBA = tetrabutylammonium ion. [c] Provided as Ph_4P·$N(CN)_2$, where Ph_4P = tetraphenylphosphonium ion. [d] All crystals are black thick plates. They are sometimes rhombic, sometimes rectangular and sometimes appear bricks at first sight. The crystals often yielded from the electrode within two days but in some cases the electrolytic solution remained unchanged for a week or two, then nucleation occurred followed by slow growth of small crystals.

Crystal Structures and Electrical Properties of STF Salts

The Octahedral Anion Salts

The octahedral anion salts all make metal-insulator (MI) transitions in the range of 170 – 270 K; their electrical behavior is shown in Figure 3.1; (a) PF_6 (T_{MI} = 175 K), (b) AsF_6 (T_{MI} = 180 K), (c) SbF_6 (T_{MI} = 265 K) and (d) TaF_6 (T_{MI} = 157 K) salts, respectively.

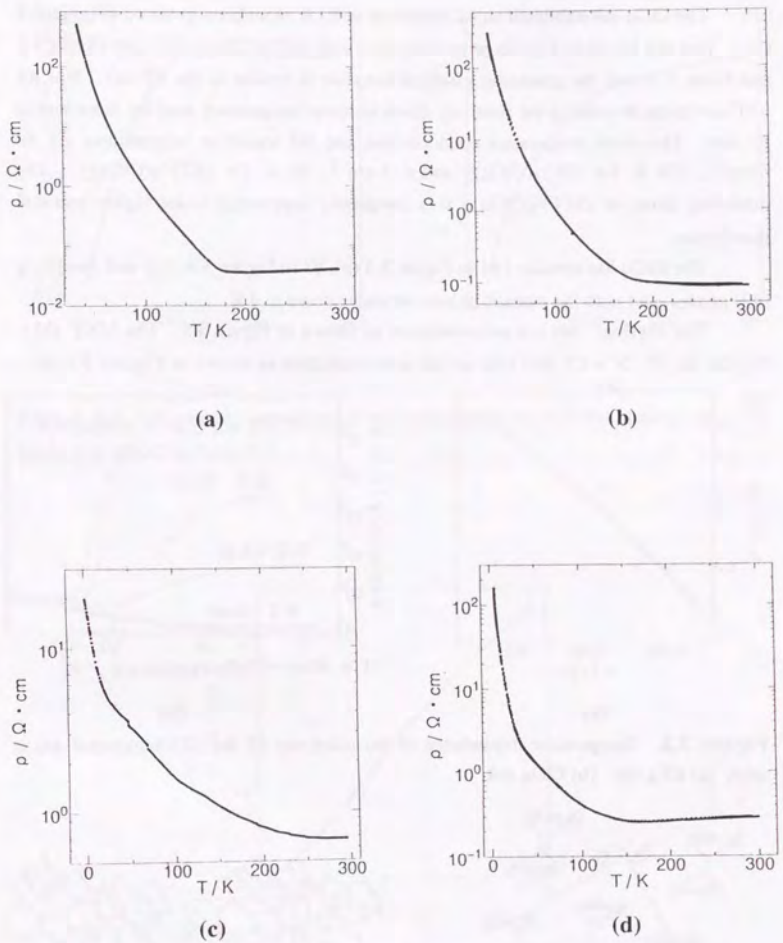


Figure 3.1. Temperature dependence of the STF/octahedral anion salts; (a) PF_6 salt, (b) AsF_6 salt, (c) SbF_6 salt, (d) TaF_6 salt

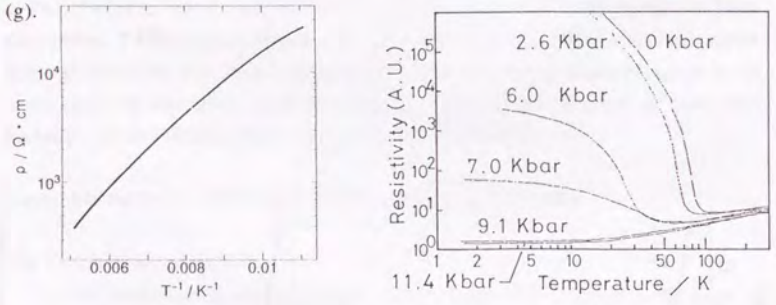
The Tetrahedral Anion Salts

The BF_4 salt is a semiconductor with an activation energy of 0.06 eV {Figure 3.2 (a)}.

The ClO_4 salt exhibited an MI transition at 80 K at ambient pressure {Figure 3.2 (b)}. This salt has turned out to be isomorphous with $(ET)_3(ClO_4)_2$ [19] (see Figure 3.3 and Table 3.2) and the qualitative electrical behavior is similar to the ET salt. But the STF salt keeps decreasing the resitivity down to lower temperature than the isostructural ET salt. The room temperature conductivities and MI transition temperatures are 50 $S \cdot cm^{-1}$, 170 K for $(ET)_3(ClO_4)_2$ and 6 $S \cdot cm^{-1}$, 80 K for $(STF)_3(ClO_4)_2$. The insulating phase of $(STF)_3(ClO_4)_2$ was completely suppressed under higher pressure than 9 kbar.

The ReO_4 has metallic {#1 in Figure 3.4 (a), #3 in Figure 3.4 (b)} and insulating (#2) phases, and both the metallic phases are stable down to 4 K.

The $HgBr_4^{2-}$ salt is a semiconductor as shown in Figure 3.5. The MX_4^- (M = Fe, Ga, In, Tl; X = Cl, Br) salts are all semiconductors as shown in Figures 3.6 (a) – (g).



(a) (b)

Figure 3.2. Temperature dependence of the resistivity of the STF/tetrahedral anion salts; (a) BF_4 salt, (b) ClO_4 salt

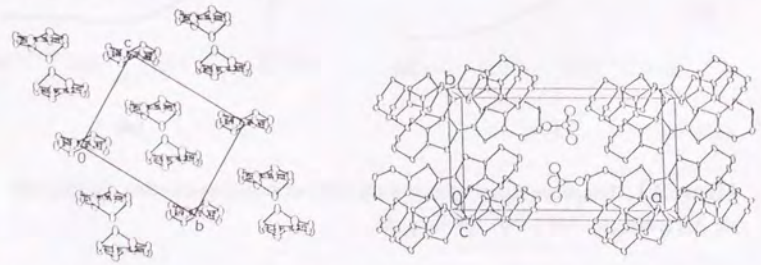
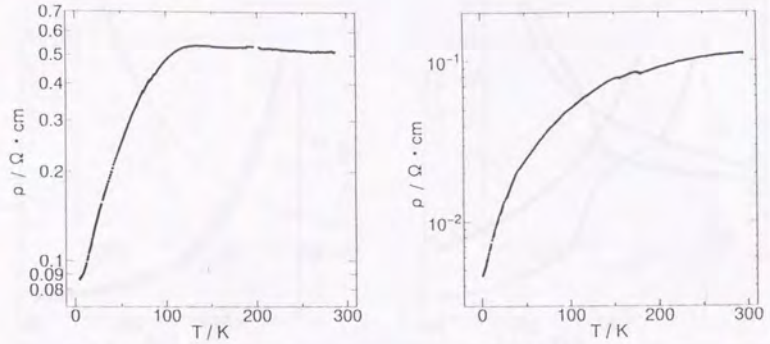


Figure 3.3. Donor arrangement (left-hand side) and crystal structure (right-hand side) of $(STF)_3(ClO_4)_2$



(a) (b)

Figure 3.4. Temperature dependence of the resistivity of the STF/ReO_4 salts; (a) #1 in Table 3.1, (b) #3 in Table 3.1

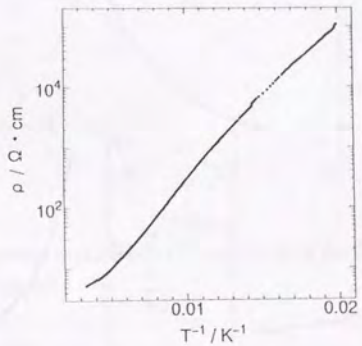
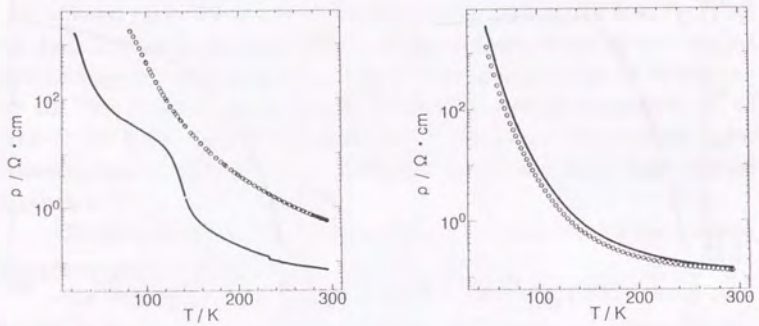
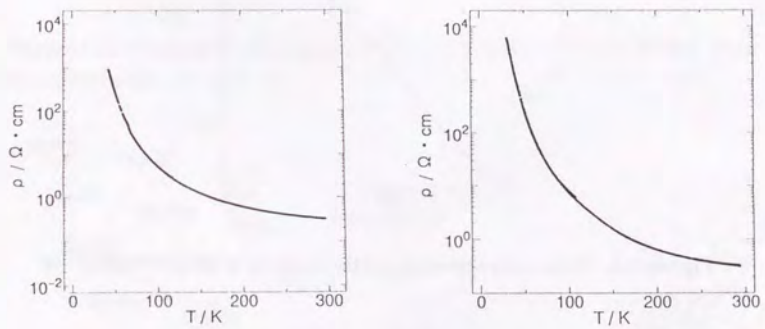


Figure 3.5. Temperature dependence of the resistivity of the STF/$HgBr_4^{2-}$salt



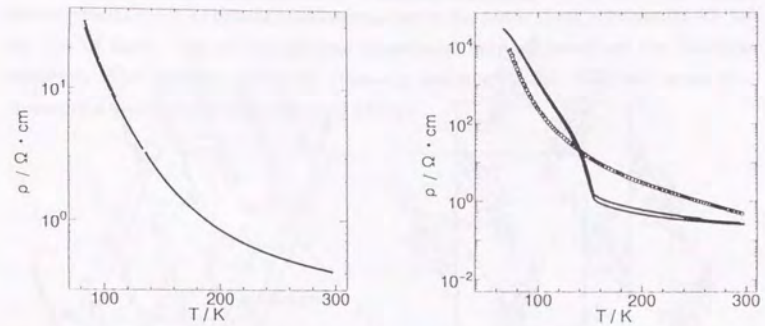
(a) (b)

Figure 3.6. Temperature dependence of the resistivity of the STF/tetrahedral anion salts; (a) κ– (line), and λ– (circle) $GaCl_4$ salts, (b) $GaBr_4$ salts: plate (circle) and needle (line)



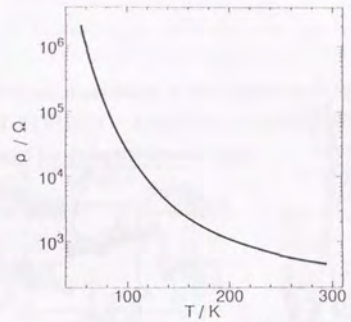
(c) (d)

Figure 3.6. Temperature dependence of the resistivity of the STF/tetrahedral anion salts (continued); (c) $InBr_4$ salt, (d) $TlCl_4$ salt



(e) (f)

Figure 3.6. Temperature dependence of the resistivity of the STF/tetrahedral anion salts (continued); (e) $TlBr_4$ salt, (f) $FeCl_4$ salts: plate (line) and needle (circle)



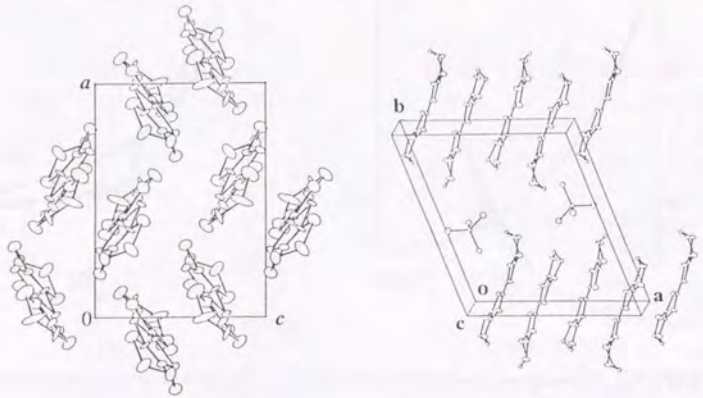
(g)

Figure 3.6. Temperature dependence of the resistivity of the STF/tetrahedral anion salts (continued); (g) $FeBr_4$ salt

The Linear Anion Salts

The linear anion yielded the widest variety of salts. The I_3 salt showed a gentle MI transition at 65 — 80 K, which X-ray study revealed to be isomorphous with α-$(ET)_2I_3$ and α-$(BETS)_2I_3$ (see Figure 3.8 and Table 3.2) and their qualitative behavior is similar to each other {Figure 3.9}. Interestingly the critical temperature and sharpness of the MI transition in α-$(STF)_2I_3$ fall into the middle of the same salts of ET and BETS. A similar result except for the T_{MI}'s was observed in diselenadithiafulvalene (DSeDTF)-

TCNQ complex [9 (b), (e)], where the donor DSeDTF is a mixture of cis- and trans-isomers and either of the isomers are different from the central part of STF.



(a) (b)

Figure 3.7. (a) Donor arrangement in κ-(STF)$_2$GaCl$_4$ and (b) Crystal structure of λ-(STF)$_2$GaCl$_4$

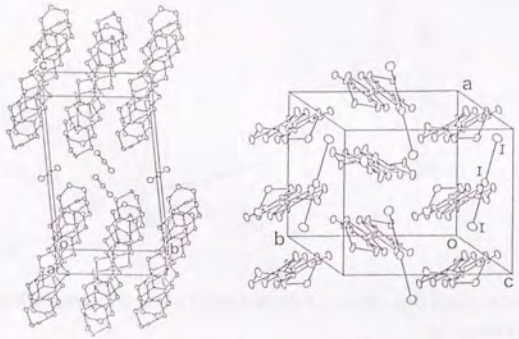


Figure 3.8. Crystal structures of α-(STF)$_2$I$_3$

The $AuCl_2^-$ salts showed two different types of behavior; metallic down to 1 K {#2 in Figure 3.10 (a)} and M-I transition at *ca.* 70 K {#1 in Figure 3.10 (b)}. As shown in Figures 3.11 (a) – (d), the latter (#1) phase has a four-fold stacking structure similar to (PT)$_2$AuCl$_2$ { PT = bis(propylenedithio)tetrathiafulvalene } (Figure 3.12) but the PT salt remains a semiconductor in all the temperature region of the measurement even under the high pressure of 14 Kbar {compare Figures 3.13 (a) and (b)}[20]. The

stacking mode of the donor molecules and an overall arrangement of the donor in the sheet are much the same with the PT salt but the STF salt has far more intermolecular short contacts (< 3.7 Å) between chalcogen atoms in the donor sheet, whereas the PT salt has few of them. The consequent two dimensional network based on the chalogen-chalcogen short contacts makes the electronic structure of the STF salt more two-dimensional and makes metallic behavior emerge.

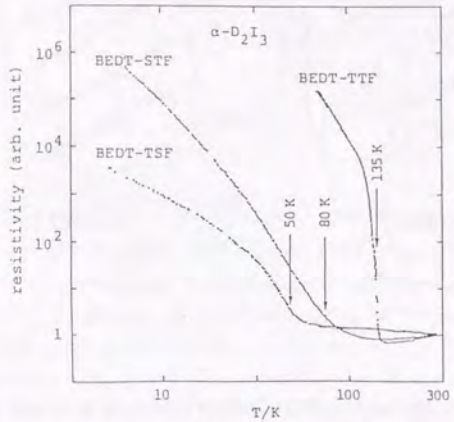
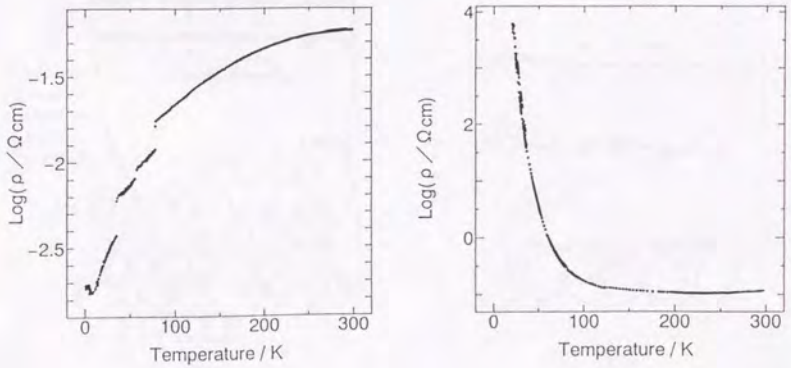
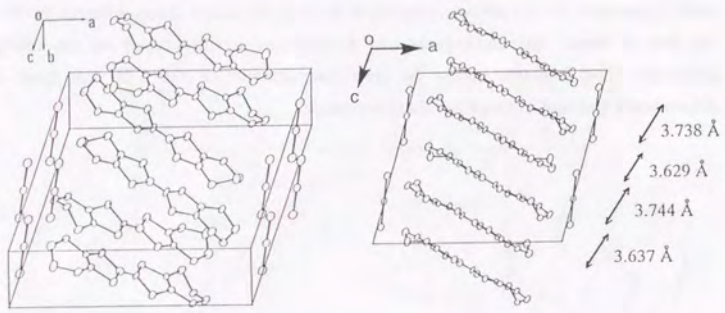


Figure 3.9. Temperature dependence of the resistivity of α-(ET)$_2$I$_3$ ("BEDT-TTF"), α-(STF)$_2$I$_3$ ("BEDT-STF") and α-(BETS)$_2$I$_3$ ("BEDT-TSF") The temperatures in the figure denote each metal-insulator transition (T_{MI}).

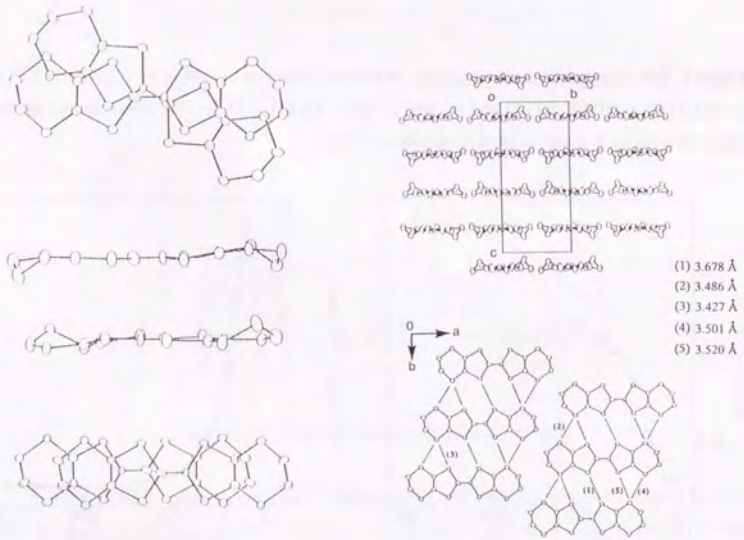


(a) (b)

Figure 3.10. Temperature dependence of the resistivity of the STF/AuCl$_2$ salts; (a) #2 in Table 3.1, (b) #1 in Table 3.1



(a) (b)



(c) (d)

Figure 3.11. (a), (b) Crystal, (c) molecular structure and (d) donor arrangement in $(STF)_2AuCl_2$

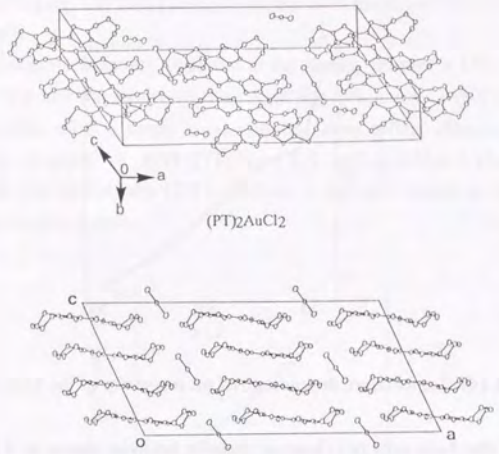
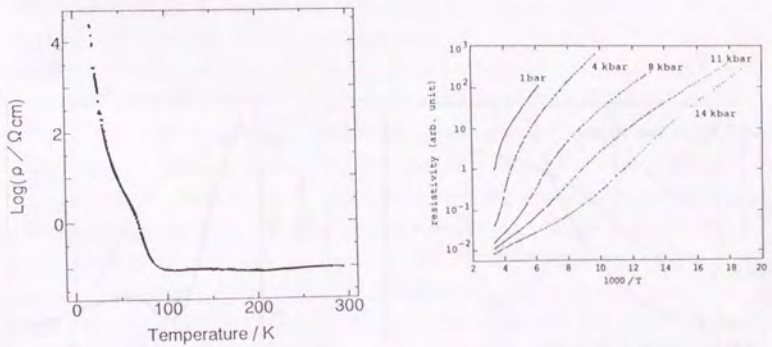


Figure 3.12. Crystal structure of $(PT)_2AuCl_2$ [20]; compare this with Figure 3.11.



(a) (b)

Figure 3.13. Temperature dependence of the resistivity of (a) $(STF)_2AuCl_2$ {#1 in Table 3.1, but a different sample from that of Figure 3.10 (b)} and (b) $(PT)_2AuCl_2$ [20]

The $AuBr_2$ salt behaved a semiconductor with an activation energy of 0.16 eV at all the temperatures of the measurement {see Figure 3.14}.

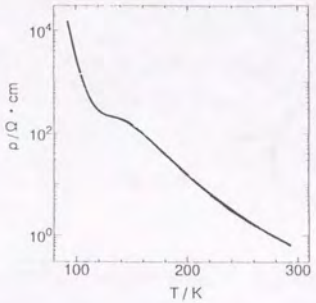
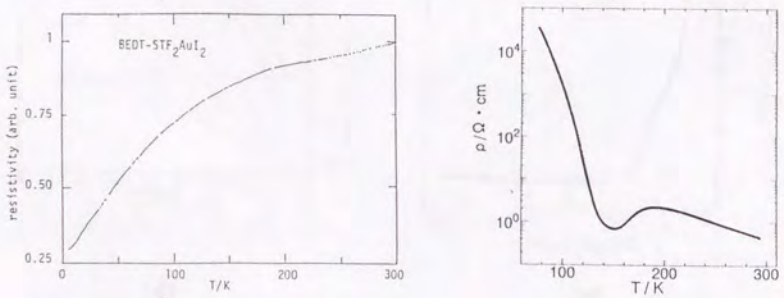


Figure 3.14. Temperature dependence of the resistivity of the STF/$AuBr_2$ salt

One of the AuI_2 salts (#1) kept its metallic behavior down to 4 K {see Figure 3.15 (a)}. This crystal has θ-type structure with lattice constants summarized in Table 3.2. The θ-type donor arrangement is a typical 2D crystal structure, which often leads to a 2D electronic structure and a stable metalic state [7 (a), 21].



(a) **(b)**

Figure 3.15. Temperature dependence of the resistivity of the STF/AuI_2 salts; (a) metallic phase (#1), (b) semiconducting phase (#2)

The $Au(CN)_2$ salt is a semiconductor with an activation energy of 0.14 eV {see Figure 3.16}.

The $Ag(CN)_2$ salt crystallized in two different [metallic {Figure 3.17 (a)} and semiconducting {Figure 3.17 (b)}] phases from the same batch, and the metallic phase is stable down to 4 K.

Some anomalous behavior observed in the $AuBr_2$ {Figure 3.14}, the AuI_2 {#2 in Figure 3.15 (b)} and the semiconducting $Ag(CN)_2$ {Figure 3.17 (b)} salts. Similar anomalous behavior with a broad maximum has been often observed in organic conductors, for example in BDT-TTP, *i.e.* 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene and related salts [23] in addition to the well-known κ-type ET salts, but the cause is yet to be known.

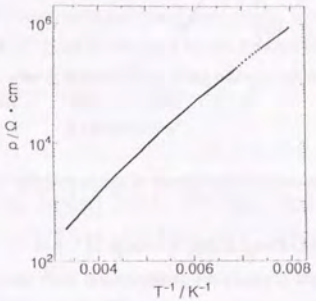
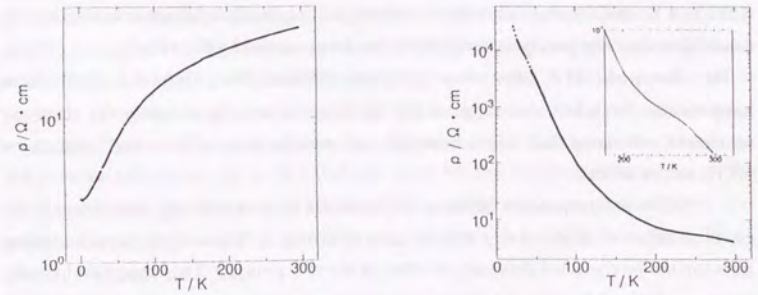


Figure 3.16. Temperature dependence of the resistivity of the STF/$Au(CN)_2$ salt



(a) **(b)**

Figure 3.17. Temperature dependence of the resistivity of the STF/$Ag(CN)_2$ salts; (a) metallic phase, (b) semiconducting phase

Other salt

The NO_3 salt behaved narrowly metallic above *ca.* 200 K with a feature around 230 K and gradually increased its resistivity at lower temperature {Figure 3.18}.

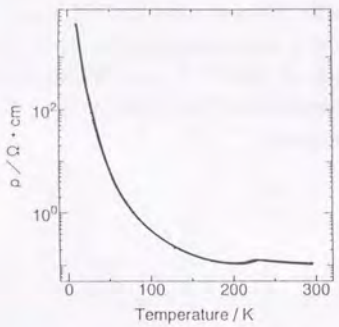


Figure 3.18. Temperature dependence of the resistivity of the STF/NO_3 salt

Grouping of the Salts: Group I and Group II

Some of the obtained crystals are isostructural with the corresponding ET and/or BETS salts, others are isostructural with neither ET salts nor BETS salts. Anyway all the STF salts examined by X-ray study were found to have an orientational disorder in the STF site. According to the extent of the effect of disorder on the electrical properties, their electrical behavior can be divided into two classes.

—The Group I salts; they exhibit clear metallic properties. Some kept their metallic states down to 4 K, and others exhibited sharp MI transitions. Such behavior indicates that the conduction electrons hardly suffer from the random potential by disorder.

—The Group II STF salts; they exhibited semiconducting behavior from room temperature. Such behavior suggests that the disorder perturbs seriously the electronic structures, otherwise they might have behaved metallic judging from the isostructural BETS and/or ET salts.

STF's unique position between BETS and ET is most evidently manifested in the electrical behavior of the charge transfer salts of Group I. Some of the semiconducting salts can not be classified definitely as either of the two groups. They may also have the same orientational disorder but their crystal structures were not analyzed and the origin of their semiconducting behavior has not yet been clear enough to attribute exclusively to disorder.

All the behavior of the Group I salts suggests that the substitution of selenium for the sulfur atoms makes intermolecular interactions closer and thus metallic phase stabler than before even when it introduces disorder in the system. In other words, the STF salts of Group I behave as if they consist of BEDT-TXF, where X is an imaginary atom that has an average radius and property between sulfur and selenium atoms though the electrical behavior is sometimes a little obscurer than the counterpart systems without disorder. This trend may enable a delicate tune of intermolecular interactions in the solid state.

Typical examples of the Group II salts are the $GaCl_4$ salts. As already shown in Figure 3.7, λ-$(STF)_2GaCl_4$ is isostructural with λ-$(BETS)_2GaCl_4$ and κ-$(STF)_2GaCl_4$ with κ-$(BETS)_2GaCl_4$; the last remains metallic down to 4 K [7 (b), (c)] and the second undergoes a superconducting transition at 8 K [7 (b), (c), 8 (a)], whilst the potential metallic nature of both STF salts have collapsed completely. In the meantime, interestingly enough, κ-$(STF)_2GaCl_4$ retains a hump around 100 K in the temperature dependence of resistivity, which seems much alike what is observed among many κ-type organic conductors.

3-4. Synthesis and Solid State Properties of the Organic Alloy System: κ-$[(ET)_{1-x}(STF)_x]_2Cu[N(CN)_2]Br$

Structure

The X-ray analysis revealed a two-dimensional array of paired π-donors (Figure 3.19) unique to the κ-type superconductors [2, 11, 24], which agreed with the literature [2 (b)]. The crystal of κ-$(ET)_2Cu[N(CN)_2]Br$ belongs to orthorhombic system with space group Pnma (a = 12.942, b = 30.016, c = 8.539 Å, Z = 4) [2 (b)]. One of the ET molecules is crystallographically independent. In the alloy system κ-$[(ET)_{1-x}(STF)_x]_2Cu[N(CN)_2]Br$ with almost identical lattice constants (e.g. #4 : a = 12.934, b = 30.070, c = 8.536 Å), ET and STF molecules are arranged in κ-type donor sites at random. Thus the large x-value involves serious disorder in the two-dimensional conduction layer. The obtained x-values, R-factors and the numbers (N) of the independent reflections {$2\theta \leq 55$ (MoK_α)} used for the structure refinements of the crystals (#1 – #5) are : #1, x = 0.0, R = 0.051, N = 1208; #2, x = 0.10, R = 0.050, N = 1947; #3, x = 0.18, R = 0.074, N = 2373; #4, x = 0.20, R = 0.061, N = 2036; #5, x = 0.63, R = 0.051, N = 1953.

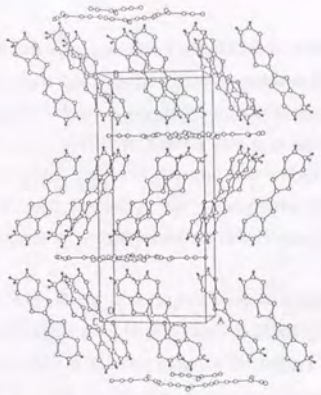


Figure 3.19. Crystal structure of κ-[(ET)$_{1-x}$(STF)$_x$]$_2$Cu[N(CN)$_2$]Br

Electrical Property

Figure 3.20 shows the temperature dependence of the electrical resistivities of the crystals of different stoichiometries. Some of them (#3, #4) do not have maxima below 100 K, which are often observed in κ-type organic superconductors [2]. The resistivity maximum becomes inconspicuous with decreasing T_c and disappears in the crystals with T_c lower than 8 K. The resistivity of the crystals without superconductivity decreases monotonously down to low temperature. An underlying mechanism of the resistivity maximum mentioned above has remained yet to be clarified, still the data demonstrated that its magnitude is related to the stability of the supercnducting phase, in other words the height of T_c.

Figure 3.21 shows the relation between T_c and x. It can be seen that increasing x lowers the T_c markedly and the superconductivity is completely suppressed within 25 % dopig of STF. The temperature dependence of the resistivity (ρ) was not simple. The system of pure phase (x = 0) exhibited a resistance maximum at 50 K, which shifted little by little to the higher temperature with increasing x and the system with large x showed a monotonous decrease of ρ.

In order to clarify the effect of the randomness, the relation between resistance ratio (RR) and T_c was examined (Figure 3.22). The RR was taken tentatively as ρ(50 K) / ρ(Tc) {or ρ(50 K) / ρ(1.5 K) in the case superconductivity was not observed} since all the samples examined exhibited metallic behavior below 50 K. The small RR implies frequent scatterings of the conduction electrons by the defects. Though its value is considered to depend on the direction along which the resistivity measurement is made, clear-cut grouping can be seen in Figure 3.22. The RR values of the system with T_c's higher than 6 K fall in the range of 6 – 9,while those with T_c's lower than 6 K have the

values around 3 and non-superconducting (down to 1.5 K) salts have the values lower than 2.5.

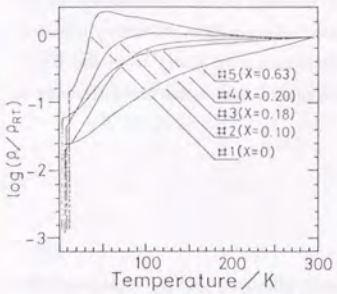


Figure 3.20. Temperature dependence of the resistivity of κ-[(ET)$_{1-x}$(STF)$_x$]$_2$Cu[N(CN)$_2$]Br with various x-values

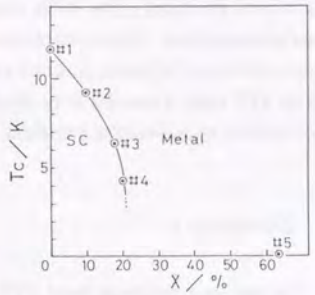


Figure 3.21. A Plot of T_c versus x-value

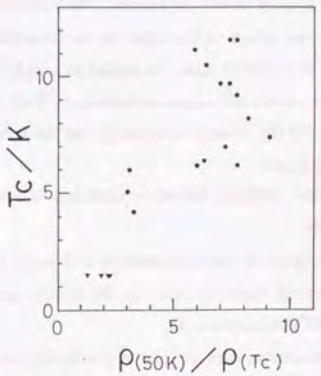


Figure 3.22. The relation between resistance ratio (RR) and T_c The RR (dot) was taken as ρ(50 K)/ρ(T_c) if superonducting transition was observed at the higher temperature than 1.5 K, otherwise (triangle) it denotes ρ(50 K)/ρ(1.5 K).

Metallic Behavior and Disorder

The Group I salts parallel the previous suggestions based on the comparison of TTF-TCNQ, DSeDTF-TCNQ and TSeF-TCNQ [10 (e)], and the solid-state properties of DSeDTF-TCNQ [10 (b), (h)]. All these results indicate that the organic metals prefer metallic states to superconducting states under perturbations like high pressure and introducing selenium atoms. Yet the STF salts have also presented the first exception: the Group II salts. Complete disruption of metallic conductivity in them in spite of the identical crystal structures to the stable metallic BETS salts can not be explained by the previous interpretations. Unless intermolecular donor interactions is extremely sensitive to a subtle difference in crystal structure and rapidly decrease in going from the BETS salts to the STF salts, it remains to be clarified what makes such a marked difference in effect of disorder upon electrical properties.

3-5. Summary

The new unsymmetrical donor STF has been synthesized and the charge-transfer salts were studied. Owing to the subtly lower symmetry of the donor, it is found to take completely random orientation in most of the solid states based on the X-ray analyses. While effect of disorder upon superconductivity is known to be serious, effect upon metallic conduction has not been regarded so serious that it may disrupt them in the organic metals. However in this study some (the Group II salts; λ-STF_2GaCl_4 and κ-STF_2GaCl_4) salts claim against such conclusion. The STF salts has the significance that it can nearly illustrate the net effect of disorder on the transport property by comparison with the corresponding ET or BETS salts. In regard to a wide variety of ET salts, which includes two-dimensional metals and superconductors as well, this work on STF salts is the first systematic study of the effects of disorder on the solid state properties without introducing other perturbations.

With respect to the relation between electrical behavior and x in κ-$[(ET)_{1-x}(STF)_x]_2Cu[N(CN)_2]Br$,

(1) The small expansion of the *b* lattice parameter and small reduction of *a* and *c* lattice parameters suggest enhanced donor overlap in the donor sheets and reduction of the intersheet interaction on STF incorporation.

(2) The conductivity measurements yielded a gentle decline in the room temperature conductivity but, at the same time, increasing stability of the metallic phases of the alloys with increasing x.

(3) The T_c rapidly decreases with increasing x and the superconductivity is completely disappeared within $x \approx 25$ %. Larger x diminishes both the resistance hump and the

resistance ratio (RR). It is also observed that the T_c enhances in accordance with the RR enhancement.

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Chapter 4.

Synthesis, Structures and Electrical Properties of The Charge-transfer Salts of 4,5-Ethylenedithio-4',5'-(2-oxatrimethylenedithio)diselenadithiafulvalene (EOST) with Linear Anions (I_3^-, IBr_2^-, ICl_2^-, I_2Br^-, $AuBr_2^-$, $Au(CN)_2^-$)*

4-1. Introduction

A few years ago Kato *et al.* reported the improved synthesis of BEDT-TSeF { bis(ethylenedithio)tetraselenafulvalene or BETS } [1]. BETS is an analogous donor of BEDT-TTF { bis(ethylenedithio)tetrathiafulvalene } but was expected to form more isotropic and thus more stable molecular metal owing to its four selenium atoms incorporated in TTF-skeleton [1]. In fact most of the charge transfer salts of BETS turned out stable metals down to low temperatures [1, 2]. In a series of BETS salts, the characteristic molecular structure of the donor { (i) rather planar (ii) five-membered and six-membered rings have even protrusions of the molecular π-orbital at the eight chalcogen atoms } [1] often results in isotropic crystal structures and intermolecular interactions. BETS is such a good donor and produces the largest fraction of the metallic salts of all the donors, unexpectedly only a few, however, have yet reported to be superconducting [3]. In terms of development of the new organic superconductors next to the ET salts, BETS is still one of the most promising building blocks among many donors. For such purpose the control of intermolecular interaction including dimensionality may be required by chemical modification. A possible approach is hybridization of the donor with an appropriate other one, where the resultant donor would inherit many features in property from both parent donors.

Nogami and co-workers reported that $(EOTT)_2IBr_2$ and $(EOTT)_2AuI_2$ retained metallic properties down to *ca.*15 K and 4.2 K, respectively [4]. The latter salt in particular sometimes reduces its electrical resistivity more rapidly in low temperatures rather than around room temperature and the resistivity ratio between 300 K and 4 K is

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over 10^2 [4]. $(EOTT)_2IBr_2$ has a stacking structure of EOTT molecules with some intercolumnar S–S contacts shorter than the van der Waals distance [4]. Accordingly the calculated electronic band structure is reported to be quasi-one-dimensional [4], which narrowly sustains a metal instability. However interesting feature is that the Fermi surface is open for the stacking direction and the substance conducts electricity along the side-by-side direction. The substitution of Se for S in TTF-skeleton would enable more close interaction in the side-by-side direction, which, in turn, would offer a more stable metallic state as demonstrated in BETS salts [1, 2]. The author expected that the title donor EOST, which is a hybrid of BETS and EOTT, could give rise to an intermediate two-dimensional electronic structure in the salts. Such a new donor even might produce new organic superconductors. Such synthetic strategy parallels the mainstream of the field and one of the most well-known successful examples is the modification of TMTTF salts into TMTSF salts. Although the solid state properties of the charge-transfer salts of another related donor molecule, OTT { bis(2-oxatrimethylenedithio)tetrathiafulvalene } [4 – 6], remain hardly known, the salts of EOST with linear anions can be expected to be good molecular conducting systems, since EOST is related more closely to EOTT rather than to OTT.

This chapter reports the solid state properties of the charge-transfer salts of a new unsymmetrical donor EOST.