

IV-D Development of Magnetic Organic Superconductors

Since the discovery of the first organic superconductor (Bechgaard salt) $(\text{TMTSF})_2\text{PF}_6$ in 1980, a grate progress has been made in the field of molecular conductors. Soon after the discovery of Bechgaard salt having one-dimensional metal nature, we tried to find a way to develop two-dimensional metals without one-dimensional metal instabilities and found the first κ -type organic superconductor with two-dimensional cylindrical Fermi surface in 1987. However, the elevation of T_c of organic superconductors has been stoped since the discovery of $\kappa\text{-ET}_2\text{Cu}[\text{N}(\text{CN})_2]\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) in 1990 and the progress of molecular design of organic metals became rather stagnant in the last 10 years.

Until recently, the fields of molecular conductors and molecular magnets have been developed almost independently with each other. But recently increasing attention has been attracted to the interplay of magnetism and conductivity in the molecular system, which began to arouse new streams in these fields. The first paramagnetic organic superconductor was found in 1995. The first antiferromagnetic organic superconductor was discovered in the last year. The recent discoveries of antiferromagnetic organic superconductors, metamagnetic organic metal, field-induced metallic states, superconductor-to-antiferromagnetic insulator transition, etc in BETS (= bis(ethylenedithio)tetraselenafulvalene) conductors seem to suggest the opening of new field of magnetic molecular conductors.

IV-D-1 BETS as a Source of Molecular Magnetic Superconductors (BETS = Bis(ethylenedithio)-tetraselenafulvalene)

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[Chem. Soc. Rev. 29, 325 (2000)]

BETS-based salts incorporating Fe^{3+} ions are most interesting candidate systems for the observation of interplay of conductivity and magnetism. Indeed, in λ - and κ -(BETS) $_2\text{FeCl}_4$, conduction electrons in the BETS layers do interact with spins localised on the FeCl_4^- anions. Since the size of non-magnetic GaX_4^- anion ($\text{X} = \text{Cl}, \text{Br}$) approximatly equal to that of FeX_4^- , (BETS) $_2\text{-GaX}_4$ system can take the crystal structure almost identical to that of (BETS) $_2\text{FeCl}_4$. Furthermore we can prepare a series of BETS conductor with mixed-metal and mixed-halogen atoms. Systematic studies on λ -(BETS) $_2\text{Fe}_x\text{Ga}_{1-x}\text{Cl}_{4-y}\text{Br}_y$ have provided a number of interesting systems, including conductors with an antiferromagnetic metal state, a metamagnetic organic metal, and an antiferromagnetic organic superconductor. Unprecedented superconductor-to-insulator transitions and superconductor-to-metal transitions have been also observed. In this report the recent our studies on the BETS systems are reviewed.

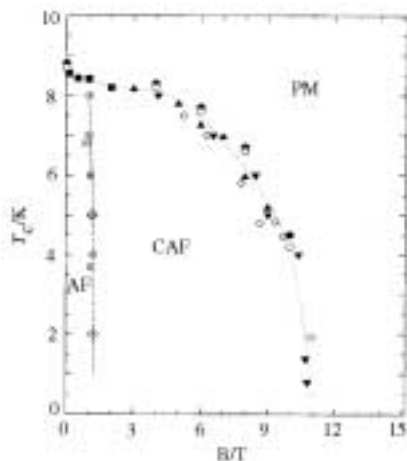


Figure 1. Temperature-magnetic field diagram of λ -(BETS) $_2\text{-FeCl}_4$.

IV-D-2 Superconductivity, Antiferromagnetism and Phase Diagram of a Series of Organic Conductors, λ -(BETS) $_2\text{Fe}_x\text{Ga}_{1-x}\text{Br}_y\text{Cl}_{4-y}$

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[Adv. Mater. 12, 1685 (2000)]

Recently a series of organic conductors based on BETS molecules and magnetic anions seem to attract an increasing interest because of their many novel properties produced by tuning the composition of the anions. They exhibit not only usual superconducting transitions but also unprecedented superconductor-to-insulator transitions. In this paper we report the electric and magnetic properties of λ -(BETS) $_2\text{Fe}_x\text{Ga}_{1-x}\text{Br}_y\text{Cl}_{4-y}$, which are strongly modified from those of λ -(BETS) $_2\text{Fe}_x\text{-Ga}_{1-x}\text{Cl}_4$ without Br atoms due to the large enhancement of electron correlation effect by $\text{Cl} \rightarrow \text{Br}$ exchange. λ -(BETS) $_2\text{Fe}_x\text{Ga}_{1-x}\text{Br}_y\text{Cl}_{4-y}$ ($x \approx 0.5$, $y = 1.0$) showed a superconducting-to-insulator transition around 2 kbar where the system takes a superconducting state at 2.5–7 K. Furthermore, a superconductor-to-metal transition, which never encountered in other organic conducting systems, was also discovered for $x = 0.1\text{--}0.2$ and $y = 1.0$. It is very interesting that the magnetic susceptibility of λ -(BETS) $_2\text{Fe}_x\text{Ga}_{1-x}\text{BrCl}_3$ shows a clear antiferromagnetic behavior even when Fe-content is very small ($x = 0.1\text{--}0.2$). The unique electric and magnetic properties reported in this paper will give a clue to clarify the role of the π -d interaction in magnetic organic superconductors.

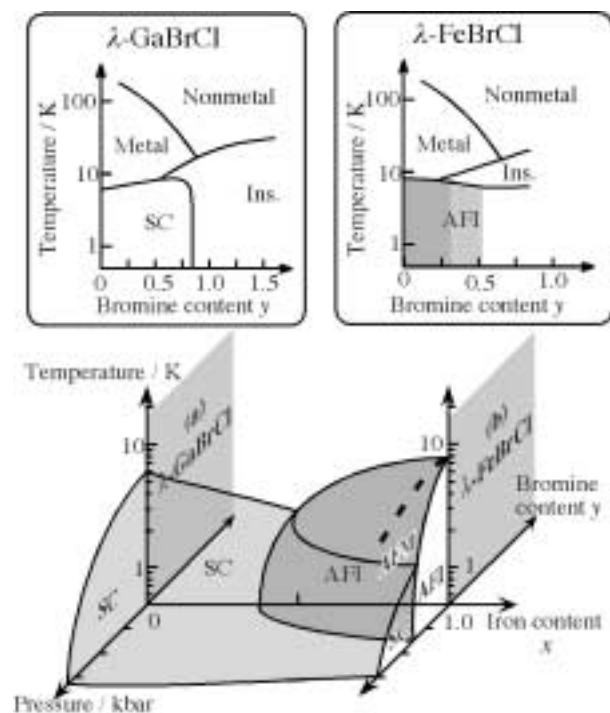


Figure 1. P - T - x phase diagrams of λ -BETS₂Fe_xGa_{1-x}Cl₄ and T - y phase diagrams of λ -BETS₂MBr_{3y}Cl_{4-y} ($M = \text{Fe, Ga}$).

IV-D-3 Fermi Surface and Phase Transition in Magnetic Field Parallel to the Conducting Plane in λ -(BETS)₂FeCl₄

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λ -(BETS)₂FeCl₄ is a very unique magnetic organic conductor having antiferromagnetic insulating ground state and exhibiting a field-restored metallic state at ambient pressure and a pressure-induced superconductivity. Shubnikov de-Haas and angular dependent magneto-resistance oscillation (AMRO) experiments were performed to study the Fermi surface. The SdH oscillations were ascribed to the two external cross sectional areas of corrugated two-dimensional Fermi surface. The cross sectional areas are estimated to be 15% and 19% of the first Brillouin zone. These results are consistent with that obtained from the AMRO measurements (17%) and also with the simple extended Hückel tight-binding band calculation reported before (see Figure 1). The resistance gradually decreases above 17 T and then becomes negligible above 19 T under magnetic fields along the direction parallel to the conduction plane. The behavior is associated with change in the magnetic torque. The results show that a phase transition is present around 18 T.

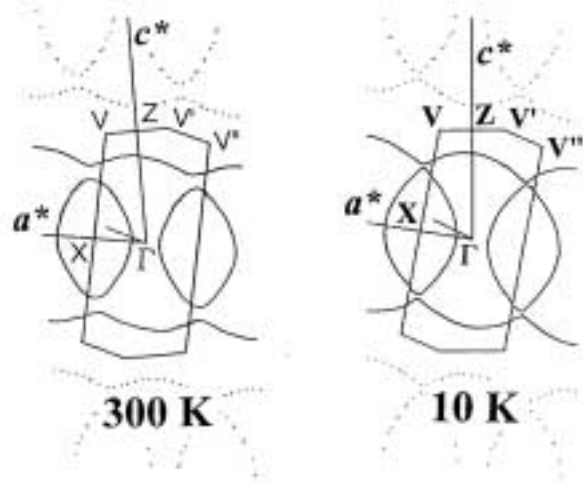


Figure 1. Cross section of calculated two-dimensional Fermi surface of λ -(BETS)₂FeCl₄.

IV-D-4 Anisotropy of Magnetic Susceptibilities of λ -(BETS)₂FeBr_xCl_{4-x}

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Owing to π - d coupling and strong electron correlation of π electron system, λ -(BETS)₂FeCl₄ takes many interesting phases such as antiferromagnetic insulating phase and field-induced ferromagnetic metal phase above 11 T. We have previously reported that the easy axis of the π - d coupled antiferromagnetic spin structure is approximately parallel to the needle axis of the crystal, that is the c axis. But recently precise torque measurements by Sasaki and Toyota suggested that the easy axis fairly deviates from the c axis. In order to confirm this, we measured magnetization by rotating one single crystal in SQUID magnetometer. As shown in Figure 1, the susceptibilities showed that the easy axis deviates from the needle axis by about 35°. The angular dependence of the magnetization of single crystal was made also on the Br-containing system λ -(BETS)₂FeBr_{0.6}Cl_{3.4}. The rotation of the easy axis by the Cl $\rightarrow$ Br exchange, which was previously reported, was confirmed.

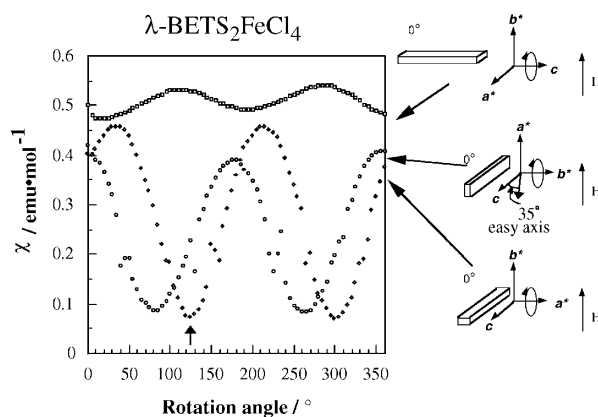


Figure 1. The angular dependence of the susceptibility of λ -(BETS)₂FeCl₄.

IV-D-5 A Novel Antiferromagnetic Organic Superconductor κ -(BETS)₂FeBr₄ [where BETS = Bis(ethylenedithio)tetraselenafulvalene]

FUJIWARA, Hideki; FUJIWARA, Emiko; NAKAZAWA, Yasuhiro; NARYMBETOV, Bakhyt Zh.; KATO, Kiyonori; KOBAYASHI, Hayao; KOBAYASHI, Akiko¹; TOKUMOTO, Madoka²; CASSOUX, Patrick³

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The electrical and magnetic properties of κ -(BETS)₂FeBr₄ salt showed that this system is the first antiferromagnetic organic metal at ambient pressure ($T_N = 2.5$ K). The characteristic field dependence of the magnetization at 2.0 K indicates a clear metamagnetic behavior. The small resistivity drop observed at T_N clearly shows the existence of the interaction between π metal electrons and localized magnetic moments of Fe³⁺ ions. In addition, this system underwent a superconducting transition at 1.1 K. The magnetic field dependence of the superconducting critical temperature cleared that the superconductivity in this system is strongly anisotropic also in the conduction plane because of the existence of the metamagnetically induced internal field based on the antiferromagnetic ordering of the Fe³⁺ 3d spins in contrast to the cases of the other conventional organic superconductors. Furthermore, the specific heat measurement exhibited a λ -type large peak corresponding to the three-dimensional antiferromagnetic ordering of high-spin Fe³⁺ ions. The lack of distinct anomaly in the C_p vs. T curve at T_c strongly suggests the coexistence of the superconductivity and the antiferromagnetic order below T_c .

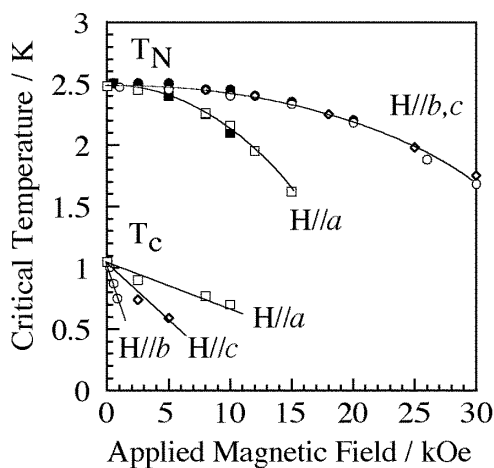


Figure 1. The H - T plots of the Néel temperatures (T_N) and the superconducting transition temperatures (T_c) under the magnetic fields applied along the three axes (squares; a -axis, circles; b -axis and triangles; c -axis) determined by electrical resistivity measurements (opened symbols) and SQUID measurements (closed symbols).

IV-D-6 The x -Dependence of Electrical Properties and Antiferromagnetic Ordering between Fe³⁺ Ions in κ -(BETS)₂FeCl_xBr_{4-x} System

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The magnetic and electrical properties of κ -(BETS)₂FeCl_xBr_{4-x} ($x = 0.1, 0.5, 1.2, 2.0, 2.3, 3.0, 3.4$ and 4.0) were examined to check the possibility of the antiferromagnetic ordering of Fe³⁺ spins and/or the possibility of superconductivity of π electron system. The temperature dependence of the magnetic susceptibility and the field (H) dependence of the magnetization (M) of κ -(BETS)₂FeCl_xBr_{4-x} at 2 K revealed that the Néel temperature shifts to lower temperature with the increase of chlorine contents. Moreover, the rotation of easy spin axis from the direction parallel to the crystal plane to the direction approximately perpendicular to the crystal plane was observed. The temperature corresponding to the small resistivity drop, which is in good agreement with the Néel temperature, shifts to lower temperature with the increase of the chlorine contents. On the other hand, the critical temperature of superconductivity shifts to lower temperature quickly with the increase of the chlorine contents ($T_c = 0.7$ K for $x = 0.1$).

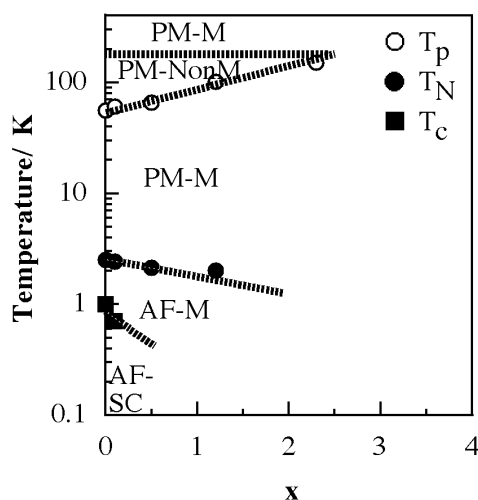


Figure 1. T - x phase diagram of κ -(BETS)₂FeCl_xBr_{4-x}. The temperature of resistivity peak (T_p) are opened circles (○), Néel temperature (T_N) are filled circles (●) and superconducting transition temperature (T_c) are filled squares (■).

IV-D-7 Successive Antiferromagnetic and Superconducting Transition in an Organic Metal, κ -(BETS)₂FeCl₄

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[Chem. Lett. 732 (2000)]

We have previously reported the crystal structures and electrical properties of κ -(BETS)₂FeX₄ ($X = \text{Cl}, \text{Br}$) systems. Unlike κ -(BETS)₂FeBr₄ exhibiting anomalous resistivity peak around 60 K, κ -(BETS)₂FeCl₄ shows a

nomal metallic behavior down to 2 K. Recently we have found κ -(BETS)₂FeBr₄ to be the first antiferromagnetic organic superconductor, which undergoes an antiferromagnetic transition at 2.5 K (T_N) and a superconducting transition at 1.1 K (T_c). A step-like resistivity anomaly at T_N gave the first direct evidence for π -d interaction between π metal electrons and localized magnetic moments in the anion sites. Since the magnitude of π -d interaction is considered to be strongly dependent on the energy level of p orbitals of halogen atoms of the anion, it may be of interest to examine precisely the susceptibility of κ -(BETS)₂FeCl₄. The *ac* magnetic susceptibility of κ -(BETS)₂FeCl₄ down to 60 mK revealed the successive phase transitions from paramagnetic metal to metallic antiferromagnet and then to superconductor which correspond to the similar transitions observed in Br-analogue λ -(BETS)₂FeBr₄. But the transition temperatures are significantly lowered ($T_N = 0.6$ K, $T_c = 0.1$ K).

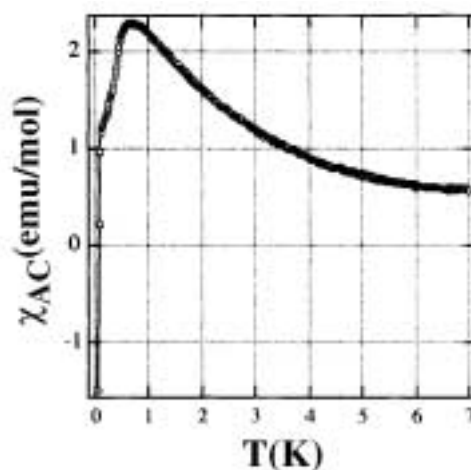


Figure 1. The temperature dependence of *ac*-magnetic susceptibility for κ -(BETS)₂FeCl₄ (polycrystalline sample).

IV-E Structural and Electrical Properties of Molecular Crystals at Low Temperature and/or High Pressure

Since the molecular crystal is very soft and rich in the structural freedom, various structural phase transitions are expected at high pressure and/or low temperature. Therefore the precise three-dimensional X-ray structure analyses at high pressure and/or low temperature are very important in the studies of solid state physics and chemistry of molecular crystals. We have examined low-temperature structures of some molecular crystals including C₆₀ molecular magnet by using low-temperature imaging plate system equipped with liquid He refrigerator. As for the structural studies at high pressure, we have continued to examine the crystal structure of molecular superconductor α -[(CH₃)₂(C₂H₅)₂N][Pd(dmit)₂]₂ exhibiting a superconductivity at 2–6 kbar. We have measured the high-pressure resistivity of (TMTTF)₂PF₆, the sulfur-analog of the first organic superconductor (TMTSF)₂PF₆ and found the superconducting transition around 52 kbar for the first time. Furthermore, we have recently succeeded to measure the resistivity of organic single crystal up to 150 kbar.

IV-E-1 Origin of Ferromagnetic Exchange Interactions in a Fullerene-Organic Compound

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[*Nature* **407**, 883 (2000)]

Almost a decade ago, the ferromagnetism of TDAE·C₆₀ (TDAE = tetrakis(di-methylamino)ethylene, $T_c = 16$ K) was reported but the origin of ferromagnetic properties of this compound has still remained mysterious. In spite of serious efforts by many research groups and suggestion that the orientations of C₆₀ molecules may be important, in the absence of structural data at low temperatures there has been little progress in the understanding of the microscopic interactions which lead to this unusual phenomenon. To resolve this problem we have performed a comparative structural study of the two different magnetic forms of TDAE·C₆₀ crystals at low temperature. Identifying the relative orientations of C₆₀ molecules as the primary variable controlling the ferromagnetic order parameter, we show

that both Ferromagnetic and low-temperature spin-glass-like ordering are possible in this material, depending on the degree of disorder.

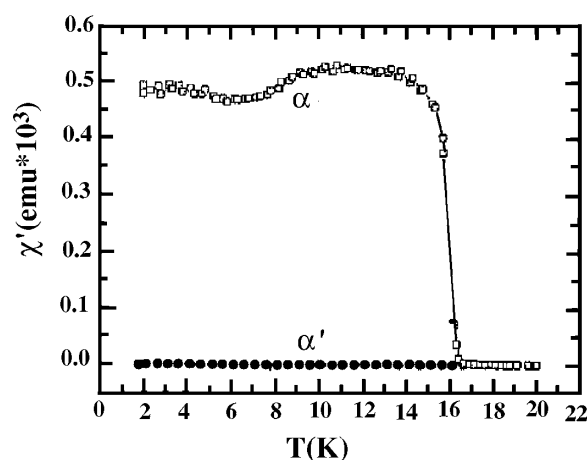


Figure 1. The *ac* susceptibility χ of paramagnetic (α') and ferromagnetic (α) sample of C₆₀·TDAE.

IV-E-2 Low temperature X-ray Crystal Structure Determination of α -(BEDT-TTF) $_2$ I $_3$ —Stripe-Like Charge Distribution at Low Temperature

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α -(BEDT-TTF) $_2$ I $_3$ is a well-known organic conductor, exhibiting a M-I transition around 135 K. Recently, the charge distribution in this compound at low temperature was investigated both theoretically and experimentally. With the aim of determining the charge distribution in this system, we performed X-ray diffraction experiments at various temperature. The reliability factor of the structure analyses (*R*) in the metallic phase was about 3% where the space group P1- was adopted. The structure analyses at 125 K and at 100K (the insulator phase) were also successfully made on the basis of the space group P1- (*R* $\approx$ 3%). However, *R*-values of the structure analyses below 75 K were higher than 6%. These results suggest the loss of inversion symmetry, in other words, the change of charge distribution at low temperature. Thus we repeated the structure analyses based on the space group P1. *R*-factor became about 3%. Figure 1 shows the temperature dependence of charges of crystallographically independent BEDT-TTF molecules estimated by using the empirical relation between bond lengths and the charge of BEDT-TTF molecule. The charges of molecule A and C were increased below 75 K, indicating the development of stripe-like charge distribution at low temperature.

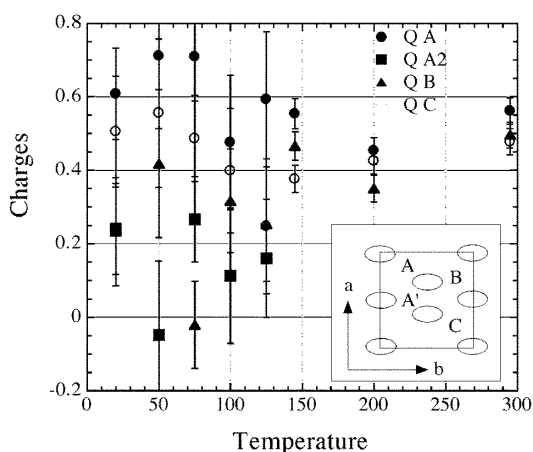


Figure 1. Temperature dependence of charge of BEDT-TTF. The inset is the schematic draw of the molecular arrangement. Molecules A and A' were related to each other by inversion symmetry in the metallic phase.

IV-E-3 Crystal and Band Structure Examinations of High-Pressure Molecular Superconductor [(C $_2$ H $_5$) $_2$ (CH $_3$) $_2$ N][Pd(dmit) $_2$] $_2$ at 10 kbar

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Based on the X-ray intensity data collected by diamond anvil cell specially designed to reduce the background X-ray diffraction from the high-pressure cell, the crystal structure of [(CH $_3$) $_2$ (C $_2$ H $_5$) $_2$ N]-[Pd(dmit) $_2$] $_2$ was determined at 10 kbar to see the origin of the peculiar *P-T* phase diagram of this molecular superconductor where the insulating phase appears at the high-pressure side of the superconducting phase. We have previously proposed a pressure-induced HOMO-LUMO “re-inversion” mechanism to explain this *P-T* phase diagram. However, it was revealed that the lattice constants is doubled along the stacking direction of Pd(dmit) $_2$ molecules above 8 kbar. This structure change is associated with the pressure-induced disorder-order transition of (CH $_3$) $_2$ (C $_2$ H $_5$) $_2$ N. The possibility of the pressure-induced HOMO-LUMO re-inversion was ruled out by the simple tight-binding band calculation based on the crystal structure determined at high pressure.

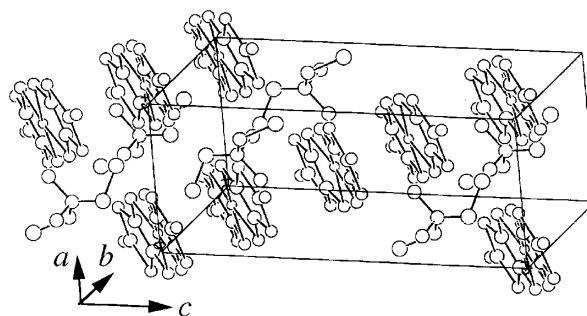


Figure 1. The crystal structure of [(CH $_3$) $_2$ (C $_2$ H $_5$) $_2$ N]-[Pd(dmit) $_2$] $_2$ at 10 kbar.

IV-E-4 Superconducting Transition of (TMTTF) $_2$ PF $_6$ above 50 kbar [TMTTF = Tetramethyltetrafulvalene]

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[*J. Am. Chem. Soc.* **122**, 3238 (2000)]

Two decades passed since the discovery of the first organic superconductor (TMTSF) $_2$ PF $_6$. However, there are many physicists and chemists who still regard TMTSF superconductor (Bechgaard salt) to be the most attractive organic conductor. Besides the superconductivity, this system exhibits novel transport phenomena related to the spin density wave (SDW) instability originated from one-dimensional nature of the electronic structure. Almost a decade ago, the generalised pressure-temperature (*P-T*) phase diagram was proposed, where all the Bechgaard salts including isostructural sulphur analogues ((TMTTF) $_2$ X (X = PF $_6$, AsF $_6$, ClO $_4$...) were located. This diagram tells us that (TMTTF) $_2$ Br and (TMTTF) $_2$ PF $_6$ become superconductors by applying 25 kbar and 35 kbar, respectively. In fact, the superconductivity of (TMTTF) $_2$ Br was discovered in 1994 (*T_c* = 0.8 K at 26 kbar). However, there have been no “TM $_2$ X systems”

whose superconductivities were confirmed in both Se- and S-analogues. We have recently succeeded to improve the technique of diamond anvil four-probe resistivity measurements and obtained the resistivity of an organic single crystal up to 150 kbar. In the course of these studies, we have found the superconducting transition of $(\text{TMTTF})_2\text{PF}_6$ above 52 kbar.

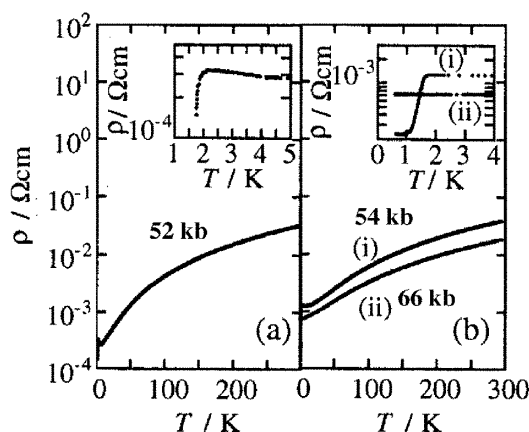


Figure 1. Resistivity of $(\text{TMTTF})_2\text{PF}_6$ at high pressure.

IV-E-5 Electrical Resistivity Measurements of Organic Single Crystals by Diamond Anvil Cell up to 15 GPa

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(¹Ehime Univ.)

At present, diamond anvil is used for very wide purpose in various high pressure experiments including resistivity measurements. In order to obtain reliable resistivity data, we must adopt the four-probe method. Since the first diamond anvil four-probe resistivity measurements by Mao and Bell, many trials have been made. However these methods seem to be inapplicable to soft organic materials. In 1985, Tozer and King reported the four-probe resistivity measurements on organic single crystal under 7.5 GPa. We have recently succeeded to obtain the accurate resistivity data of organic single crystal up to 15 GPa. The diamond anvil

cell was the essentially the same to that designed by Takemura more than 20 years ago. The size of the needle-shaped single crystal was about 0.25 mm in length. Inconel T301 was used as a gasket and annealed gold wires were used as leads, which were fixed to the single crystal by gold paints. An example of the pressure dependence of the resistivity is given in Figure 1.

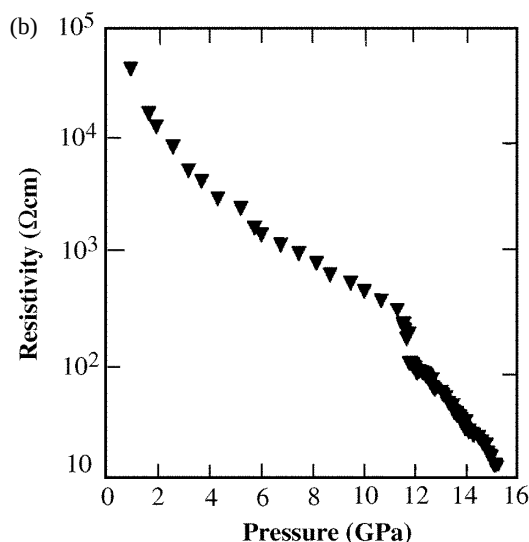
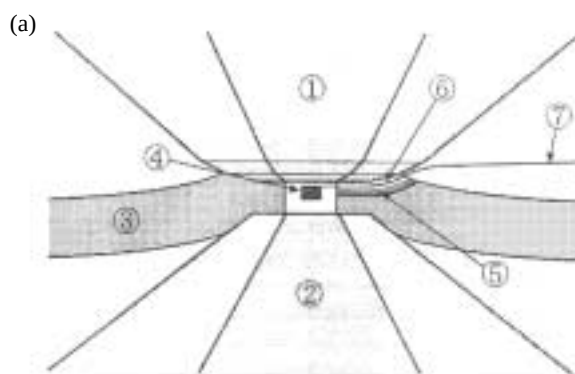


Figure 1. (a) Schematic drawing of sectional view around the sample. (b) Pressure dependence of the resistivity of the crystal of TMTTeN.

IV-F Development of New Functional Molecular Materials

Molecule can be regarded as the smallest nano-system where various functions can be assembled. The development of new molecules will be the most important driving force for further development of materials chemistry. Although the development of fruitful systems has been still continued in the field of molecular metals, we have to grow out of the conventional molecular conductors. Two main targets of our present studies are (1) molecular metals and superconductors composed of single-component molecules and (2) pure organic magnetic metals. Very recently, we have succeeded to prepare the first single-component molecular metal. Based on the idea on the construction of metal band by using multi-sulfur planar π molecules developed by us in 1980s, the neutral Ni complex molecules having extended TTF-ligands were synthesized. Very simple crystal structure, closely packed molecular arrangement and metallic behavior of this system show that the boundary between “molecular crystal” and “metallic crystal” was removed by this finding.

IV-F-1 A Three-Dimensional Synthetic Metallic Crystal Composed of Single Component Molecules

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(¹Univ. Tokyo)[*Science* **291**, 285 (2001)]

Since the discoveries of semiconducting properties of phthalocyanine and condensed aromatic hydrocarbons around 1950 and the discoveries of one-dimensional molecular metals around 1970, many chemists have dreamed to design single-component and/or three-dimensional molecular metals composed of planar molecules. Especially, the design of single component molecular metal had been one of the final goals of the chemists in this field. Although three-dimensional metals and superconductors have been already realized by the discoveries of alkali-metal C₆₀ complexes around 1990, the single component molecular metals remained to be developed up to 2000. Preparation, crystal structure analysis and resistivity measurements of the crystal of [Ni(tmdt)₂] (tmdt = trimethylenetetrafulvalenedithiolate) molecule revealed that the first metallic crystal composed of single component molecules was discovered. [Ni(tmdt)₂] crystal retained metallic state down to 0.6 K. The compact three-dimensional molecular arrangement and the tight-binding electronic band structure calculation showed the system to be not only the first single-component molecular metal but also the first three-dimensional synthetic metal composed of planar molecules.

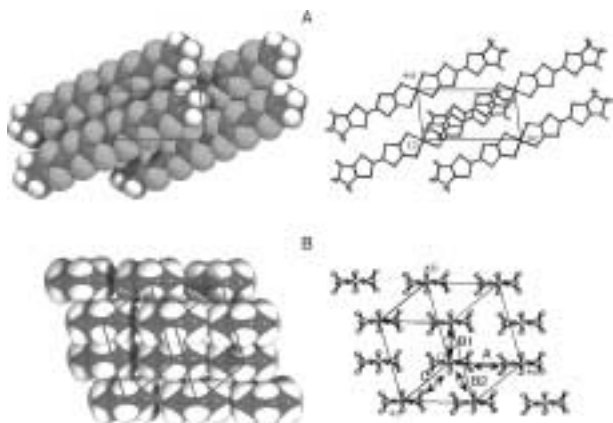


Figure 1. The crystal structure of [Ni(tmdt)₂].

IV-F-2 Development of Single-Component Molecular Metals Based on Transition Metal Complexes with Extended-TTF Dithiolate Ligands

TANAKA, Hisashi; KOBAYASHI, Hayao; KOBAYASHI, Akiko¹
(¹Univ. Tokyo)

Novel molecular conductors composed of neutral transition metal complex molecules with extended TTF-like ligands, ptdt, dmdt and tmdt were developed (M = Ni, Pd, Pt, Cu, Co, Au; ptdt = propylenedithiotetrafulvalenedithiolate, dmdt = dimethyltetrafulvalene-dithiolate and tmdt = trimethylenetetrafulvalenedithiolate). These molecules have extended π conjugated systems. The synthetic works were made under strictly inert atmosphere because these metal

complexes were very sensitive to oxygen. By electrochemical oxidation, black microcrystals of the neutral complexes were obtained, which showed very high conductivities (compaction pellet): [Ni(dmdt)₂], 200–400 Scm⁻¹; [Pd(dmdt)₂], 100 Scm⁻¹; [Co(dmdt)₂], 1–2 Scm⁻¹. The molecular conformations and magnetic properties were revealed to be dependent on the central metal atoms.

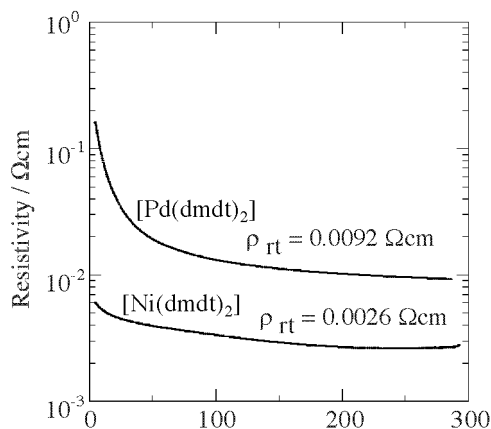


Figure 1. Temperature dependence of the resistivities of [M(dmdt)₂] (M = Ni, Pd) (compaction pellet).

IV-F-3 Synthesis and Properties of a New Organic Donor Containing a TEMPO Radical

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In the course of the development of new types of organic conductors, the interests have been focused on the molecular conductors and superconductors containing magnetic transition metal anions for the investigation of the interplay between the conductivity and magnetism. On the other hand, several attempts have been performed using donors containing a stable TEMPO or NN radical to investigate the interaction between conduction electrons of the charge-transfer complex and localized spins of the organic stable radical parts for the development of novel organic conducting-magnetic multifunctional materials and organic ferromagnetic metals. Among them, very recently we have synthesized a new donor containing a TEMPO radical, TEMPOET, and investigated the physical properties of its cation radical salts. Herein we report the synthesis and physical properties of a new TEMPO-containing electron donor **1** in which a TEMPO radical part connects to the EDT-TTF skeleton through a pyrrolidine ring. The ESR spectra of **1** indicated three absorption lines ($g = 2.0062$, $a_N = 15.5$ G) characteristic of TEMPO radical. The donor **1** is paramagnetic and showed antiferromagnetic interaction at low temperature region ($\theta = -2.4$ K). The CV measurement revealed **1** shows two pairs of reversible redox waves (+0.48 and +0.86 V vs. Ag/AgCl) and one oxidation wave (+0.83 V).

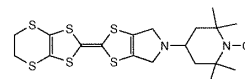


Figure 1. Structure of **1**.

IV-F-4 Synthesis, Structures and Properties of an New TSeF Derivative Containing Pyrazino-Ring and Its Cation Radical Salts

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In the search for new molecular conductors, enhancement of the intermolecular interaction by the condensation of hetero ring and the substitution of chalcogen atoms is considered to be very important to realize two-dimensional metals. From this viewpoint, we had synthesized a novel unsymmetrical donor containing pyrazino-ring: PEDTTSeF and reported the crystal structures and physical properties of its cation radical salts. Several of them showed metallic conducting behavior down to low temperatures due to their interesting zig-zag β'' -type two-dimensional donor arrangements and strong side-by-side interaction between the chalcogen atoms and nitrogen atoms. We have also synthesized the other novel TSeF derivative containing pyrazino-ring: pyrazino-TSeF. The donor shows two pairs of reversible redox waves (+0.79 and 1.14 V vs. Ag/AgCl in PhCN). The oxidation potentials are slightly positively shifted compared with those of BETS (+0.70 and +0.97 V) under identical conditions. According to the crystal structure analysis, the stoichiometry of the ClO_4^- salt was determined to be 1:1 (D:A) (Figure 1). The cation radical salts were prepared by electrolytic oxidation. The ClO_4^- and PF_6^- salts are semiconductors, due to a 1:1 stoichiometry at least in respect of the ClO_4^- salt.

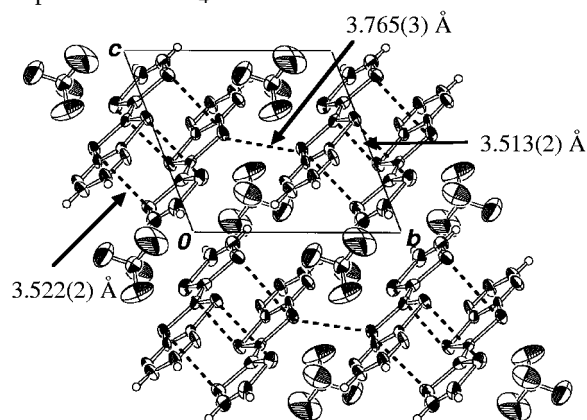


Figure 1. Crystal structure of the ClO_4^- salt of pyrazino-TSeF.