IV-C Development of Multi-Functional Molecular Conductors

The molecules are usually assembled by weak intermolecular interactions and tend to retain their isolated electronic states even in the crystalline state. Consequently, the multi-functional systems may be constructed by assembling various molecules with different characters. Thus, the molecules are considered to be suitable building blocks for the bottom-up construction of the systems where various functions coexist and interplay with each other.

Recently, "dual-action system" such as magnetic molecular conductors has attracted a considerable interest. Though there exist well-known systems such as the paramagnetic organic superconductor and the ferromagnetic organic metals, there seems almost no significant interactions between conduction parts and magnetic parts. In contrast, we have discovered several novel organic superconductors exhibiting remarkable electro-magnetic properties originating from π-*d* coupling. κ-$(BETS)_2FeBr_4$ and κ-$(BETS)_2FeCl_4$ are the first and the second antiferromagnetic organic superconductors, respectively. Furthermore, κ-$(BETS)_2FeBr_4$ exhibits a metamagnetic (antiferromagnetic → ferromagnetic) transition around 1.6 T to give rise to a sharp switching behavior between superconducting and metallic states by tuning the external field around 1.6 T. In addition, due to the π-*d* interaction, a field-induced superconducting transition was observed around 12.5 T. But this is not the first observation of field-induced superconductivity in the organic conductors. We have previously reported the field-induced superconductivity in λ-$(BETS)_2FeCl_4$. Owing to the relatively large π-*d* interaction, λ-$(BETS)_2FeCl_4$ shows the field-induced superconductivity around 33 T, though the ground state is a π-*d* coupled antiferromagnetic insulating state. Moreover, the analogous system with diluted magnetic moments, λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ $(0.35 < x < 0.5)$ undergoes the successive metal → superconductor → insulator transitions with decreasing temperature. The electromagnetic properties of these BETS conductors gave clear examples of organic conductors showing the π-*d* coupling. Besides these conductors, we have recently tried to develop another type of magnetic molecular conductors by using the π donor molecules incorporating stable organic radicals. When the magnetic anions such as $FeCl_4^-$ are adopted as counter anions, the magnetic organic conductors with two kinds of spin systems will be prepared where a variety of novel electromagnetic properties will be expected.

Until quite recently, it has been long believed that all the molecular metals are constructed of more than two chemical species because the intermolecular charge transfer phenomena have been used to generate charge carriers. The best example may be the first organic superconductor, $(TMTSF)_2PF_6$ where the hole carriers are generated in TMTSF columns by the charge transfer from TMTSF to PF_6^- ($TMTSF \rightarrow TMTSF^{+0.5}$). Due to the charge transfer, the molecular metals have the character of ionic crystals. But we have recently developed molecular metals consisting of neutral single-component molecules where intermolecular charge transfer cannot be considered. More recently, the experimental evidence for the existence of Fermi surfaces in this single-component molecular crystal was obtained. The discovery of the single-component molecular metal disclosed the amphibious molecular crystal consisting of neutral single-component molecules and possessing 3D Fermi surfaces.

IV-C-1 Highly Conducting Crystals Based on Single-Component Gold Complexes with Extended-TTF Dithiolate Ligands

SUZUKI, Wakako[1]; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]; FUJISHIRO, Yuichi[2]; NISHIBORI, Eiji[2]; TAKATA, Masaki[2]; SAKATA, Makoto[2]; FUJIWARA, Hideki; KOBAYASHI, Hayao
([1]Univ. Tokyo; [2]Nagoya Univ.)

[*J. Am. Chem. Soc.* **125**, 1486 (2003)]

We have recently found the first metallic crystal consisting of neutral transition metal complex molecules with extended-TTF (tetrathiafulvalene) ligands, $[Ni(tmdt)_2]^{0+}$ (tmdt = trimethylenetetrathiafulvalenedithiolate) with metallic behavior down to very low temperature. In terms of valence electrons, the neutral bis(dithiolato)gold complex is isoelectronic to the planar bis(dithiolato)nickel monoanion complex with one unpaired electron per molecule, which makes the electromagnetic properties of the neutral gold complex very attractive. It has been thought that these unpaired electrons or holes in the bis(dithiolato)gold complexes have a possibility to form a metallic band. We have prepared the crystals composed of single-component gold complexes with extended-TTF ligands, $[Au(dmdt)_2]^{0+}$ (dmdt = dimethyltetrathiafulvalenedithiolate) and $[Au(tmdt)_2]^{0+}$ and examined their structural, electrical and magnetic properties. Since the crystals were very small, the synchrotron radiation X-ray powder experiments were performed by using the imaging plate detectors and the Large Debye-Scherrer camera at the facility SPring-8 BL02B2. Although the sufficient diffraction patterns could not be obtained on $[Au(dmdt)_2]$, an ideal X-ray powder pattern was obtained on $[Au(tmdt)_2]$, which revealed $[Au(tmdt)_2]$ to be isostructural to $[Ni(tmdt)_2]$. The crystal structure was successfully analysed by a self-consistent iterative analysis of a combination of the maximum entropy method (MEM) and Rietveld analysis. The lattice constants of $[Au(tmdt)_2]$ are: $a = 6.4129(1)$ Å, $b = 7.5514(2)$, $c = 12.1543(3)$, $\alpha = 90.473(3)°$, $\beta = 96.698(2)$, $\gamma = 103.008(3)$, $V = 569.21(2)$ Å^3. The high conductivity of compacted crystalline powder sample (≈ 15 S cm^{-1} at room temperature) and the XPS and NEXAFS measurements suggested $[Au(tmdt)_2]$ to be essentially a metal. The temperature dependence of ESR intensity showed that $[Au(tmdt)_2]$ undergoes a magnetic transition around 100 K with keeping the highly conducting states. To our knowledge, there has been no molecular conductor exhibiting magnetic transition at the temperature as high as 100 K. The SQUID measurements suggested the magnetic transition to be antiferromagnetic one.

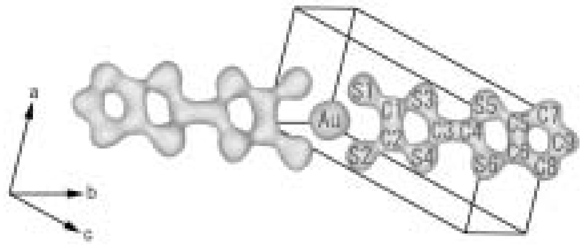
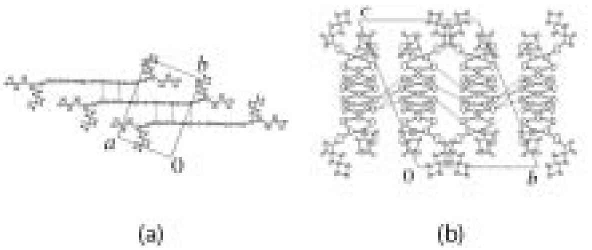


Figure 1. Structure of [Au(tmdt)$_2$] determined by MEM/Rietveld analysis of X-ray powder patterns.

IV-C-2 Structure and Physical Properties of Palladium Complexes with Extended-TTF Dithiolate Ligands

SUZUKI, Wakako[1]; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]; HASEGAWA, Ami[2]; MIYAMOTO, Takeshi[2]; KOBAYASHI, Hayao
([1]Univ. Tokyo; [2]Kitasato Univ.)

In the course of the studies on the development of single-component molecular metals, new dithiolato palladium complexes with an extended-TTF (tetrathiafulvalene) ligand (^{n}Bu$_4$N)[Pd(C3-tdt)$_2$](**1**) and [Pd(C3-tdt)$_2$] ((C3-tdt)$^{2-}$ = dipropylthiotetrathiafulvalenedithiolate)(**2**) were prepared and their crystal structures were determined. The electrochemical properties of **1** were investigated by cyclic voltammetry technique at 20 °C and scan rate of 200 mVs^{-1}. The cyclic voltammogram measured in dimethylformamide showed three pairs of reversible redox waves. The first, second and third potentials are –0.92, –0.30 and +0.47 V *vs.* Ag/AgCl, respectively. The first, second and third waves correspond to three electrons, two electrons and one electron oxidation, respectively, leading [Pd(C3-tdt)$_2$]$^{2-}$ to [Pd(C3-tdt)$_2$]$^{4+}$. The crystal structures of **1** and **2** were examined. **2** has three-dimensional S···S short contacts even though **2** has large steric hinderence through large propylthio groups. The molecular structure is almost planar except for four propylthio groups and more planar than that in **1**. The magnetic susceptibility of (^{n}Bu$_4$N)[Pd(C3-tdt)$_2$] gave good agreement with Bonner-Fisher model (J = –16 K), which suggests [Pd(C3-tdt)$_2$] anions form approximately a one-dimensional antiferromagnetic chain. On the other hand neutral [Pd(C3-tdt)$_2$] was found to be a semiconductor with a room temperature conductivity of 10^{-2} S·cm^{-1}.



(a) (b)

Figure 1. Crystal structure of [Pd(C3-tdt)$_2$] (**2**) projected onto (a) the *ac*-plane and (b) the *bc*-plane.

IV-C-3 Single-Component Molecular Crystal with Three-Dimensional Fermi Surfaces

TANAKA, Hisashi[1]; TOKUMOTO, Madoka[1]; ISHIBASHI, Shouji[1]; GRAF, David[2]; CHOI, Eun S.[2]; BROOKS, James S.[2]; YASUZUKA, Shyuma[3]; OKANO, Yoshinori; KOBAYASHI, Hayao; KOBAYASHI, Akiko[4]
([1]AIST; [2]Florida State Univ.; [3]Natl. Inst.Mater. Sci.; [4]Univ. Tokyo)

Recently a considerable attention has been attracted to the unconventional conducting molecular systems such as single component molecular conductors, nanowires, molecular wire junctions and even DNA. Though the intriguing reports on new types of molecular systems are rapidly increasing in number, there seem to be many systems whose origins of the charge carriers and/or transport mechanisms still remain unclear. The single-component molecular crystal, we reported recently, consisting of neutral metal complex molecules [Ni(tmdt)$_2$] (tmdt = trimethylenetetrathia-fulvalenedithiolate) exhibits metallic behavior down to 0.6 K, but without Fermiological evidence of metallic nature. In order to prove definitely the existence of an amphibious molecular crystal consisting of single-component neutral molecules and possessing metal electrons, the torque magnetometry measurements of de Haas van Alphen oscillatory signals in a single crystal of [Ni(tmdt)$_2$] were performed by using a sensitive microcantilever at low temperatures in high magnetic fields to 45 T. Because of very small size of the crystals (of order 130 × 100 × 20 μm^3, and 0.5 μg in mass), we employed a commercial microcantilever for atomic force microscope (AFM). A simple resistance bridge circuit was used to cancel the background resistance of the two piezoresistive sensing cantilevers on the AFM assembly. The observed signals for all directions of magnetic field revealed unambiguously the presence of three-dimensional Fermi surfaces for both electrons and holes, which correspond well to the band structure calculated by local density approximation (LDA) and *ab initio* plane-wave norm-conserved pseudopotential method.

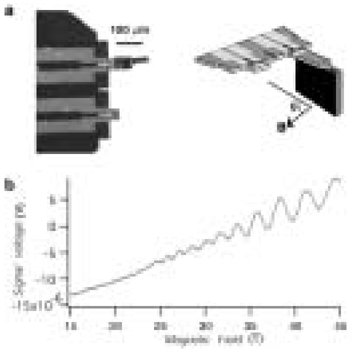


Figure 1. (a) AFM cantilever for torque magnetometry, (b) The raw torque magnetometer signal *versus* the applied magnetic field showing de Haas van Alphen oscillation of the single-component molecular metal, Ni(tmdt)$_2$.

IV-C-4 Infrared Electronic Absorption in Single-Component Molecular Metal

KOBAYASHI, Akiko[1]; SASA, Masaaki[1]; SUZUKI, Wakako[1]; FUJIWARA, Emiko[1]; TANAKA, Hisashi[2]; TOKUMOTO, Madoka[2]; OKANO, Yoshinori; FUJIWARA, Hideki; KOBAYASHI, Hayao
([1]Univ. Tokyo; [2]AIST)

[*J. Am. Chem. Soc.* in press]

It is commonly accepted that the electronic energy of a molecule is much higher than the vibrational energy of a molecule. If a molecule with electronic excitation in the *infrared* (*ir*) region can be designed, then the molecular system is expected to have unprecedented electronic properties. In order to develop a metallic crystal consisting of single-component molecules, we have tried to synthesize molecules with unprecedentedly low electronic excitations (or unprecedentedly small HOMO-LUMO gaps). In fact, as reported before, we could find the first single-component molecular crystal with stable metallic state down to 0.5 K. If our molecular design is correct, the transition metal complex molecules with extended TTF ligands (L) will have very small HOMO-LUMO gap. We have synthesized and examined the electronic absorption spectra of the crystals of $M(L)_2$[M = Ni, Pd; L = tmdt (trimethylenetetrathiafulvalenedithiolate), dmdt (dimethyl-tetrathiafulvalenedithiolate), ptdt (propylenedithiotetrathia-fulvalenedithiolate) and dt (tetrathiafulvalenedithiolate)]. Since a suitable solvent was not found, the *visible* (*vis*) and *ir* spectra were measured on crystalline powder samples. $Ni(tmdt)_2$ and $Ni(dmdt)_2$ exhibited the broadest absorption maxima around 2200 cm^{-1}. To our knowledge, this is the smallest electronic absorption energy ever reported for single-component closed-shell molecular systems. Although the electronic absorptions around 2200 cm^{-1} of $Ni(tmdt)_2$ and $Ni(dmdt)_2$ seem to suggest an extremely small HOMO-LUMO gap, the $M(L)_2$ peaks blue shifted as the semiconducting properties of the crystal increased, which indicates that the band structure plays a crucial role. Based on the extended-Hückel tight-binding band parameters, the electronic spectra were calculated. The good agreement between observed and calculated spectra shows that the single-component molecular conductors are composed of molecules with unprecedentedly small HOMO-LUMO gaps.

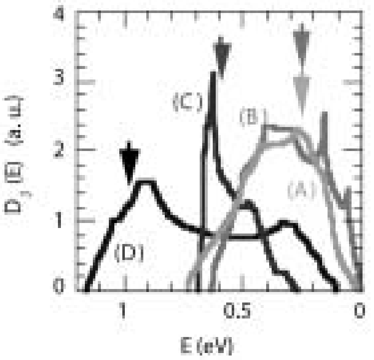


Figure 1. The calculated joint density of states $D_J(E)$: (A) $Ni(tmdt)_2$, (B) $Ni(dmdt)_2$, (C) $Ni(ptdt)_2$, and (D) $Pd(dt)_2$. The *E*-dependence of $D_J(E)$ is consistent with the observed electronic absorption spectra for each system. The arrows indicate the energy of observed absorption maxima.

IV-C-5 A Novel TTP Donor Containing a PROXYL Radical for Magnetic Molecular Conductors

FUJIWARA, Hideki; LEE, Ha-Jin; KOBAYASHI, Hayao; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

[*Chem. Lett.* 482 (2003)]

The development of new electron donors for molecule-based conductors involving a magnetic centre are of quite interest to investigate the interplay between the π conducting electrons generated by an oxidation and the localized radical spins, and several donors containing a stable radical have been synthesized to try for novel conducting-magnetic bifunctional materials. Among them, to realize the metallic conductivity, we focused on the molecules with TTP skeleton [TTP = 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene], which was regarded as a series of promising donors for the realization of stable metallic states. We synthesized a novel electron donor consisting of the TTP framework and a stable PROXYL radical part **1** and cleared its structure and physical properties. Furthermore, we reported the physical properties of its ClO_4^- and $FeCl_4^-$ salts. Among them, the $FeCl_4^-$ salts of **1** (D:A ratio ≈ 1:0.46) showed the highest conductivity record (1.1 S cm^{-1}) in the cation radical salts based on the donors containing stable organic radicals reported so far, even though it was measured on compressed pellets. This salt showed semiconducting behavior, however, the activation energy is quite small value of 0.02 eV. Therefore, the electrical conductivity of this salt can be considered to be essentially metallic if we could measure the conductivity using its single crystals. The χT values of this salt around room temperature correspond to the sum of the contributions from one PROXYL radical, high spin Fe^{3+} and conduction electrons, suggesting the coexistence of these three different magnetic moments. These results indicate that this salt is possibly the first example of paramagnetic organic metal with the coexistence of the conduction electrons and two kinds of the localized spins.

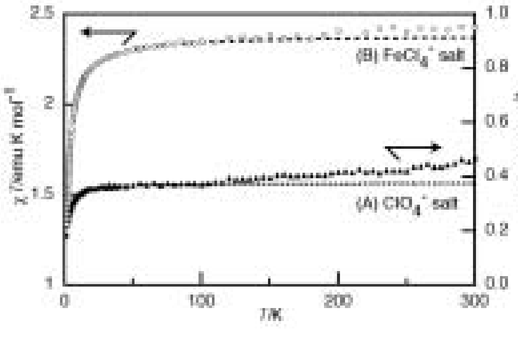


Figure 1. Magnetic properties of the cation radical salts of **1**.

IV-C-6 Synthesis, Structures and Physical Properties of a New Organic Conductor Containing a Stable PROXYL Radical

FUJIWARA, Hideki; LEE, Ha-Jin; CUI, Heng-Bo; KOBAYASHI, Hayao; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

We have reported several π-extended donor molecules containing a stable organic radical part, and recently, we have discovered highly conducting cation radical salts by use of the bis-fused TTF skeleton called as TTP containing a PROXYL radical substituent. However we could not clear the crystal structures of the cation radical salts based on such TTP-based donor molecules because it was difficult to obtain suitably large crystals for crystallographic analysis so far. Very recently, we succeeded in the structure analysis of a quite small crystal of the AsF_6^- salt of a newly synthesized cyclopenteno-fused TTP derivative **1** carrying a stable PROXYL radical part by using a new X-ray diffractometer equipped with the confocal X-ray mirror system and the CCD detector. The AsF_6^- salt has a 4:1 stoichiometry of D:A. As shown in Figure 1, the TTP skeleton of the donor molecules formed the π-conduction layer along the *ab*-plane and the PROXYL radical parts of both the donors and the AsF_6^- anions formed the insulating layers sandwiched by the donor layers. The donor layer has a quite unique structure and each the donor molecules (A and B) constructed independent one-dimensional stackings I and II in the donor layer. Reflecting strong one-dimensionality of the intermolecular interactions along the *b*-axis, the calculated Fermi surface also indicates the one-dimensional electronic structure of this salt. Above 100 K, the χT values are larger than the value for one $S = 1/2$ spin per one donor molecule (0.375 emu K mol^{-1}), suggesting a small contribution from conduction electrons. That is, the localized spin of the PROXYL radical part and π conduction electrons seem to coexist at higher temperature. This salt showed relatively high room temperature conductivity of 1 S cm^{-1} and semiconducting temperature dependence of resistivities with a very small activation energy of 0.046 eV.

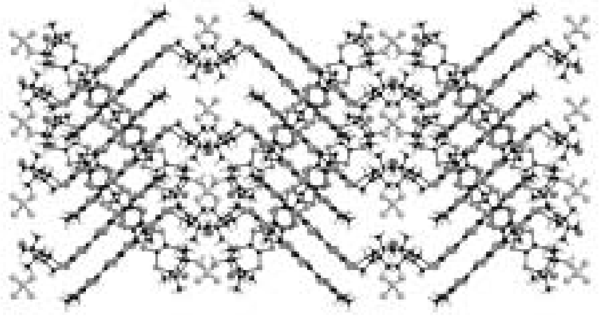


Figure 1. (a) Crystal structure of the AsF_6^- salt of **1** projected on to the *bc*-plane.

IV-C-7 Crystal Structures and Physical Properties of New Magnetic Conductors Based on π-Donor Molecule Containing a Stable Organic Radical

LEE, Ha-Jin; CUI, Heng-Bo; FUJIWARA, Hideki; KOBAYASHI, Hayao; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

In the research for new molecular-based organic conductors, a considerable interest has been focused on the development of molecular conductors and superconductors containing magnetic transition metal anions to investigate the intrerplay between conduction electrons and localized magnetic moments in organic conductors. From this point of view, several donors containing a stable organic radical part such as TEMPO and NN, have been prepared with the aim of developing novel organic conducting-magnetic multifunctional materials and organic ferromagnetic metals. We have recently reported highly conducting radical salts, for example, the $FeCl_4^-$ (1:0.46) salt (σ_{RT} = 1 Scm^{-1}) of the donor (TTP-proxyl (**1**)) based on the bi-fused TTF skeleton named as TTP containing a PROXYL radical. However we could not solve the crystal structure of these cation radical salts because it was impossible to obtain single crystals suitable for crystallographic analysis. In this paper, we reported the preparation of the $FeCl_4^-$ and $GaCl_4^-$ salts of the donor **1**, which have a 1:1 stoichimoetry, and examined their structure, and magnetic and conductivity properties. Overall temperature dependence of the **1**·$FeCl_4$ indicates typical semiconducting behavior with an activation energy of *ca.* 0.13 eV. The room temperature electrical conductivity of this salt is low, with a value of about 10^{-3} Scm^{-1}, due to the 1:1 stoichiometry and strongly dimerized structure. The χT value of **1**·$FeCl_4$ at room temperature is 4.65 K·emu·mol^{-1} and slightly lower than 4.75 K·emu·mol^{-1} expecting from the sum of the contribution form one PROXYL radical ($S = 1/2$; 0.375 K·emu·mol^{-1}) and high spin Fe^{3+} ($S = 5/2$; 4.375 K·emu·mol^{-1}), and the value slightly increases as temperature decreases to 50 K.

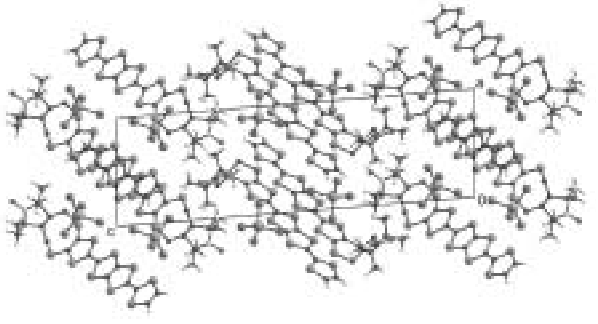


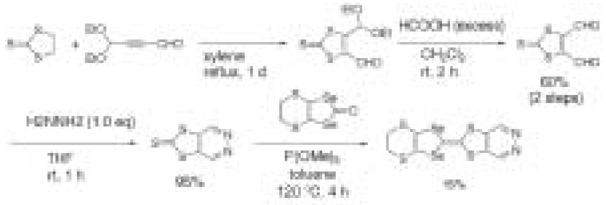
Figure 1. Crystal structure of the $FeCl_4^-$ salt of **1** projected onto the *ac*-plane.

IV-C-8 An Unsymmetrical Donor Fused with Pyridazine Ring

OTSUBO, Saika; TAKAHASHI, Kazuyuki; CUI,

Heng-Bo; FUJIWARA, Hideki; KOBAYASHI, Hayao; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

We have reported that the interaction between π conduction electrons and *d* magnetic anions plays an important role to realize novel electro-magnetic properties such as unprecedented superconductor-to-insulator transition and magnetic field-induced superconductivities of λ- and κ-type BETS salts containing high-spin Fe^{3+} ions. In order to enhance the interaction between donor and anion layers, we have prepared an EDST analogue fused with a pyridazine ring. The new thione unit, pyridazino-1,3-dithiole-2-thione was synthesized in 57% yield (3 steps). The new donor (**1**) was prepared by a phosphite-mediated cross-coupling reaction of the thione unit with 4,5-ethylenedithio-1,3-diselenol-2-one in 16% yield (Scheme 1). The cyclic voltammogram shows one reversible and one irreversible waves. The first and the second oxidation potentials were +0.86 and +1.21 V *vs.* Ag/AgCl, respectively. The crystal structure of the ReO$_4^-$ salt showed that the D:A ratio was 1:1 and the donor molecules formed dimer with a head-to-tail overlap mode. There were anions between the donor dimers and no columnar structure was observed.



Scheme 1. Synthetic route of **1**.

IV-C-9 Structural, Electrical and Magnetic Properties of a Series of Molecular Conductors Based on BDT-TTP and Lanthanoid Nitrate Complex Anions [BDT-TTP = 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6- tetrathiapentalene]

CUI, Heng-Bo; OTSUKA, Takeo; KOBAYASHI, Akiko[1]; TAKEDA, Naoya[1]: ISHIKAWA, Masayasu[1]; MISAKI, Yohji[2]; KOBAYASHI, Hayao
([1]Univ. Tokyo; [2]Kyoto Univ.)

[*Inorg. Chem.* **42**, 6114 (2003)]

The crystals of a series of novel molecular conductors, which are based on π donor molecules BDT-TTP [2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene] with a tetrathiapentalene skeleton and lanthanide nitrate complex anions [Ln(NO$_3$)$_x$]$^{3-x}$ (Ln = La, Ce, (Pr), Tb, Dy, Ho, Er, Tm, Yb, and Lu) with localized 4*f* magnetic moments, were synthesized. Except for the Ce complex, the salts were composed of (BDT-TTP)$_5$[Ln(NO$_3$)$_5$] and were isostructural. Even though the Ce crystal had a different composition, (BDT-TTP)$_6$[Ce(NO$_3$)$_6$](C$_2$H$_5$OH)$_x$ ($x \approx 3$), the crystals all had the space group, $P\bar{1}$. Previously, we reported the crystal structures and unique magnetic properties of (BDT-TTP)$_5$[Ln(NO$_3$)$_5$](Ln = Sm, Eu, Nd, Gd). Thus by combining the results of this work with previous one, we for the first time succeeded to obtain a complete set of organic conductors composed of the identical π-donors (BDT-TTP in this case) and all the lanthanide nitrate complex anions (except the complex with Pm^{3+}). The crystals were all metallic down to 2 K. Electronic band structure calculations resulted in two-dimensional Fermi surfaces, which was consistent with their stable metallic states. Except the Lu complex, which lacked paramagnetic moments, the magnetic susceptibilities were measured on the six heavy lanthanide ion complex salts by a SQUID magnetometer (Ln = Tb, Dy, Ho, Er, Tm, and Yb). The large paramagnetic susceptibilities, which were caused by the paramagnetic moments of the rare-earth ions, were obtained. The Curie-Weiss law fairly accurately reproduced the temperature dependence of the magnetic susceptibilities of (BDT-TTP)$_5$ [Ho(NO$_3$)$_5$] in the experimental temperature range (2–300 K) and a comparatively large Weiss temperature ($|\theta|$) was obtained [θ(Ho) = –15 K]. The fairly strong intermolecular magnetic interaction between Ho^{3+} ions, which was suggested by the $|\theta|$-value, is inconsistent with the traditional image of strongly localized 4*f* orbitals shielded by the electrons in the outer 5*s* and 5*p* orbitals.

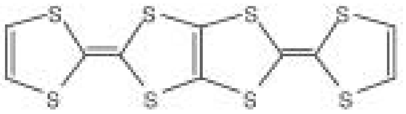


Figure 1. BDT-TTP [2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene].

IV-C-10 Anomalous 1:1 Salt with Metallic State down to 15 K, (BETS)GaBr$_4$

CUI, Heng-Bo; OKANO, Yoshinori; FUJIWARA, Hideki; KOBAYASHI, Hayao; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

Except for a few conductors such as (TTM-TTP)I$_3$ with metallic state down to 160 K, almost all the 1:1 salt of π donors (D) and inorganic anions (A) have been considered to become insulators due to the large on-site Coulomb interactions. However, we have recently found a 1:1 salt of BETS (= bis(ethylenedithio)tetraselenafulvalene) and GaBr$_4^-$ with high room-temperature conductivity of about 20 S cm^{-1}. The resistivity decreased slowly but almost linearly with lowering temperature and increased rapidly below *ca.*15 K (T_{MI}). That is, (BETS)GaBr$_4$ is the anomalous 1:1 salt with stable metallic state down to about 15 K. The crystal has a very simple and unique structure. The lattice constants are: a = 7.050 Å, b = 8.489, c = 24.142, α = 85.63°, β = 83.79, γ = 68.85, V = 1338.5 Å^3, Z = 1. Similar to usual organic metals with the composition of D$_2$A, the crystal contains donor and anion layers. But due to 1:1 stoichiometry, the donor and anion layers are arranged as, DAADAA··· along the *a* direction. Considering the Coulomb repulsion between anions, this arrangement seems to be very unusual. In fact, (BETS)FeBr$_4$ has a completely different molecular arrangement, despite that the 2:1 salts of $(BETS)_2FeBr_4$ and $(BETS)_2GaBr_4$ take the isomorphous structures to each other. Band structure calculation gave 2D electron and hole Fermi surfaces. ESR measurements suggested that the spin susceptibility, line width and *g*-value change their temperature dependencies around T_{MI}. The susceptibility increased below T_{MI} shows the low-temperature insulating state to be paramagnetic.

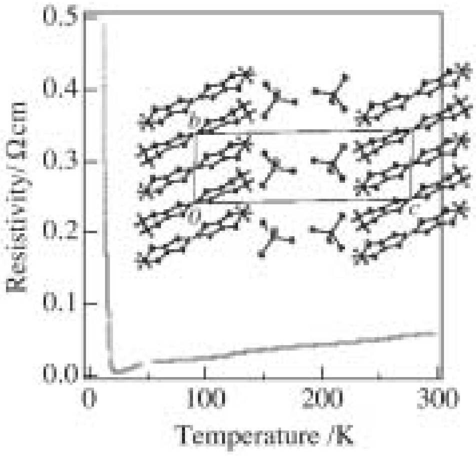


Figure 1. Crystal structure and temperature dependence of resistivity of $(BETS)GaBr_4$.

IV-C-11 High Pressure Effect on Conducting Behavior of an Antiferromagnetic Superconductor κ-$(BETS)_2FeBr_4$

OTSUKA, Takeo; FUJIWARA, Hideki; KOBAYASHI, Hayao; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

κ-$(BETS)_2FeBr_4$, were found to show a unique successive phase transition from paramagnetic metal to antiferromagnetic metal to antiferromagnetic superconductor with lowering temperature. Recently, even the magnetic field induced superconductivity was discovered around 12.5 T. In order to acquire the key to solve the mechanism of these unique electro-magnetic properties, we measured the conduction behavior of this complex under high pressure.

At ambient pressure, a kink anomaly of the resistivity was observed at 2.4 K which is related with the Néel order of Fe^{3+} moments. Resistivity decrease at 1.4 K corresponds to the onset of superconducting phase transition. The pressure dependencies of T_N and T_C (onset) are summarized in Figure 1. The gradual increase of T_N could be attributed to the contraction of the lattice, which will be consequent on the increase of the magnetic interactions. On the other hand, the T_C decreases with increasing pressure, and around 3.5 kbar sharply shifted off lower than 0.6 K, which is the lowest measurement temperature. It is normal that the superconducting phase is suppressed by pressure, because of the stabilization of metallic state at high pressure. Although our preliminary experiments up to 15 T could not find the onset of reentrant field-induced superconducting state, the high-pressure resistivity behaviors under magnetic field will be informative for the understanding of the superconductivity of this unique *d*-π system.

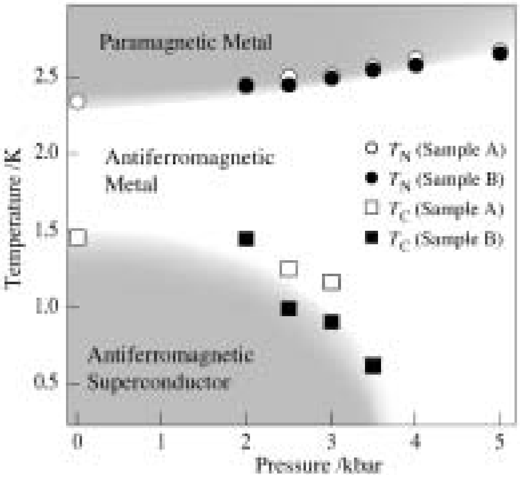


Figure 1. Pressure-temperature phase diagram of κ-$(BETS)_2FeBr_4$.

IV-D Development of Multi-Functional Porous Molecular Materials

The synthesis of new materials with new functions is the most important driving force for advancing molecular material sciences. The molecules are the smallest functional units of the materials and have been regarded as suitable building brocks for the bottom-up construction of multifunctional nano-systems. Recently, a large interest seems to be concentrated to the development of new functional molecular systems. Though increasing numbers of various intriguing molecular conducting systems such as molecular wires, atomic wires embedded in nano-porous molecular materials, molecular wire junctions and even DNA have been reported recently, there seems to be many systems whose underlying sciences seem to be very ambiguous. On the other hand, physics and chemistry of the bulk systems with typical electronic functions such as molecular superconductors and molecule-based magnets have been intensively studied in the last two decades. The *bi*functional molecular systems such as magnetic organic conductors have been developed by combining π donor molecules responsible for the electron conduction and magnetic anions, from which novel molecular systems exhibiting remarkable electro-magnetic properties such as field-induced superconductivity and switchable superconductivity coupled with metamagnetism of the anion part, have been discovered recently. However, an innovative progress seems to be needed for further studies on the traditional molecular conducting systems. The recent progress in the development of the supramolecular systems seems to suggest a way to develop completely new types of multi-functional molecular systems. Nanoporous supramolecular systems have aroused rapidly growing interest because of their abilities on the constructions of potential hydrogen storage materials, gas sensors, molecular nano-devices, *etc*. We have recently launched to try to develop new molecular systems with multi-functionality by combining nano-porous frameworks and suitable guest molecules.

IV-D-1 Manganese(II)-Formate–a 3D Porous Homometallic Ferrimagnetic Diamond Network with Nodes of Mn-Centered $MnMn_4$ Tetrahedron

WANG, ZheMing; ZHANG, Bin; FUJIWARA, Hideki; KOBAYASHI, Hayao; KURMOO, Mohamedally[1]
([1]*Inst. Physique Chimie Matériaux Strasbourg)*

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Microporous coordination framework solids with high stability have been the focus of intense research activity because of their potential applications, associated with the porosity, in many fields. Chemists have been trying to add functionalities in addition to the porosity, such as magnetism, to these materials; thus new multifunctional materials are expected. We have examined a new form of metal(II)-formate. The novel 3D porous homometallic ferrimagnets based on manganese(II) with formate as the connector, $[Mn_3(HCOO)_6](CH_3OH)(H_2O)$ **1**, its desolvated form $[Mn_3(HCOO)_6]$ **2**, and the dioxane-inclusion compound **3**. Formic acid is the smallest and simplest carboxylic acid. It can form either a one-atom or a three-atom connector. The materials show a highly stable, unprecedented diamondoid framework based on octahedrally coordinated Mn-centered $MnMn_4$ tetrahedral nodes, and display porosity for guest exchange and 3D long-range magnetic ordering. At room temperature, **1** has a χT value of 12.41 cm^{3}Kmol^{-1}. The behavior is that of a ferrimagnet, with a minimum in χT at 21 K. The minimum χT reaches 6.53 cm^{3}Kmol^{-1} at 21 K then gradually rises to 12.24 cm^{3}Kmol^{-1} at 11.5 K. After that it rises sharply to the maximum of 374.4 cm^{3}Kmol^{-1} at 7.0 K. This work demonstrates a new, simple and easy approach to obtain magnetically porous materials.

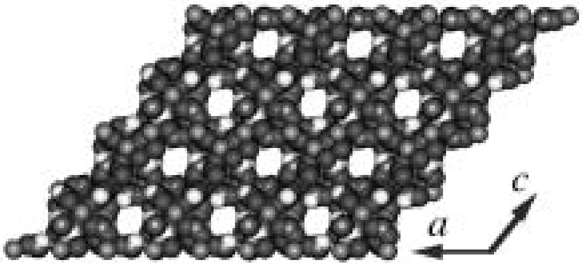

Figure 1. The space filling view of the framework with empty channels. The channels are occupied by methanol and water in **1** or dioxane in **3**.

IV-D-2 Magnetic Coordination Network Embedded in Polyiodide Matrix

WANG, ZheMing; ZHANG, Bin; OTSUKA, Takeo; FUJIWARA, Hideki; KOBAYASHI, Hayao; FUJIWARA, Emiko[1]**; YAN, Chunhua**[2]
([1]*Univ. Tokyo;* [2]*Peking Univ.)*

Crystal engineering of coordination networks has become a rapidly developing research area because of its importance in fundamental research and producing novel smart materials. Various bridging ligands have been employed to construct coordination networks. When they are neutral, the resultant networks are positive. Thus counter charged parts, *i.e.*, anions, coordinating directly to metal ions or acting as guest, are necessary to keep the whole system neutral, which have a strong influence on determining the structures of the produced network. Sometimes, the positive coordination networks can provide temprates for the formation of anion frameworks to produce, for example, novel organic-inorganic hybrid materials). However, to the best of our knowledge, polyiodides, a class of interesting and unique anionic species, have never been introduced in the crystal engineering of coordination networks.

In this work, we employ 4,4'-bipyridine-N,N'-dioxide (dpdo) to build the first series of architectures with positive coordination network and polyiodide, $[M(dpdo)_3](I_7)_2$, **1**, **2**, **3**, and **4** for M = Mn, Co, Ni, and Zn respectively, and examined their unusual structural and magnetic properties. All the compounds are isomorphic. As expected, the structure is composed of positive three-dimensional coordination network $[M(dpdo)_3{}^{2+}]_\infty$ of six-connected M nodes and the heptaiodide I_7^- anions. The Mn, Co, and Ni compounds show weak ferromagnetism due to anti-symmetric exchange interaction between magnetic metal ions. The critical temperatures, T_c's, are 5.7, 4.8 and 8.2 K for **1**, **2** and **3**, respectively. Thus, we have successfully developed a series of new magnetic and non-magnetic compounds by the assembly of positive coordination network with polyiodide through the concept of crystal engineering. The compounds with M^{2+} ions (M = Mn, Co, Ni) exhibit not only unusual structural characteristics, *i.e.*, the interwoven of 3D coordination network with polyiodide matrix, but also weak ferromagnetism.

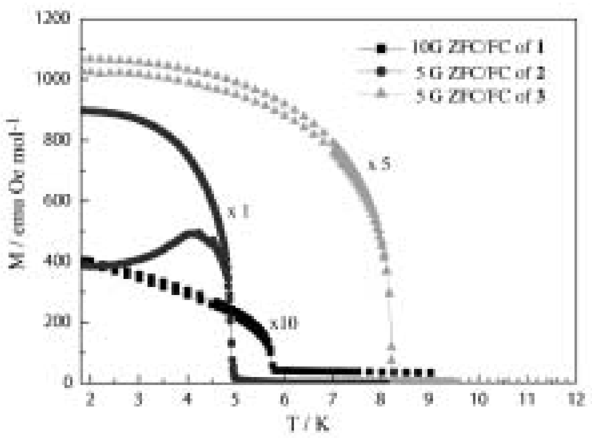

Figure 1. Zero-field (ZFC) and field-cooled (FC) *M-T* under low-field for **1**, **2** and **3**.