

IV-C Development of Multi-Functional Molecular Systems

Various types of molecular conductors such as organic superconducting alloys containing localized magnetic moments, single-component molecular metals with unprecedentedly high antiferromagnetic transition temperature, molecular conductors exhibiting resistivity anomaly coupled with a spin transition, and ferro- and ferri-electric porous molecular crystals were developed and their physical properties were examined. Recently, magnetic molecular conductors have attracted a considerable interest because of their possible *bi*-functional properties originated from the interaction between π conduction electrons and localized magnetic moments. But except BETS (bis(ethylenedithio)tetrathiasfulvalene) conductors with FeX_4^- ($X = \text{Cl}, \text{Br}$) anions developed more than ten years ago, there has been almost no organic superconductor (and even metal) exhibiting distinct *bi*-functional properties. In the last ten years, we have discovered unprecedented organic superconductors such as the system exhibiting “superconductor \rightarrow insulator transition,” the antiferromagnetic organic superconductors and the field-induced organic superconductors. We have recently re-examined the temperature-composition phase diagram of the alloys of organic superconductor $(\lambda\text{-(BETS)}_2\text{GaCl}_4)$ and field-induced organic superconductor $(\lambda\text{-(BETS)}_2\text{FeCl}_4)$ and found that the superconducting temperature phase of the alloy is stabilized by neighbouring on the antiferromagnetic insulating phase. In addition, we have reconfirmed the recently discovered peculiar “constant resistivity state” between zero-resistivity (or superconducting) state and normal metal state. It will be highly expected that new “vortex dynamics” will be disclosed in future from this unprecedented organic superconducting alloy.

Besides BETS conductors, we have developed new types of magnetic conductors such as (1) single-component molecular metal where conduction electrons and antiferromagnetic order coexists below 110 K, (2) novel system exhibiting weakly metallic behavior at high temperature and weak ferromagnetic properties at low temperature and (3) molecular conductors consisting of π molecule responsible for electron conduction and spin-crossover transition metal complex counter ion. We are also trying to synthesize new organic donors with stable radical spin parts and new functional porous molecular crystals.

We reported the improved method of four-probe resistivity measurements using diamond anvil several years ago. However we had to stop the high-pressure experiment since then. But we are now re-trying to perform the single-crystal resistivity measurements above 20 GPa.

IV-C-1 Phase Diagram and Anomalous Resistivity Behavior of $\lambda\text{-(BETS)}_2\text{Fe}_x\text{Ga}_{1-x}\text{Cl}_4$

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Rich variety of organic conductors provides unique chances to encounter novel systems showing unexpected conducting phenomena such as a superconductor-to-insulator (SC-I) transition and organic thyristor effect. Several years ago, we have reported that $\lambda\text{-(BETS)}_2\text{FeCl}_4$ undergoes a field-induced superconducting transition, where BETS (= bis(ethylenedithio)tetraselenafulvalene, $\text{C}_{10}\text{H}_8\text{S}_4\text{Se}_4$) is a π donor molecule. Since the size of FeCl_4^- anion is almost equal to that of GaCl_4^- , unprecedented alloys $(\lambda\text{-(BETS)}_2\text{Fe}_x\text{Ga}_{1-x}\text{Cl}_4)$ of organic superconductor ($\lambda\text{-(BETS)}_2\text{FeCl}_4$) and field-induced organic superconductor can be prepared at arbitrary mixing ratio. We have previously reported the temperature-composition (T - x) phase diagram of $\lambda\text{-(BETS)}_2\text{Fe}_x\text{Ga}_{1-x}\text{Cl}_4$. However, we have recently found that x -value shows a significant difference even in one single crystal, which requested careful re-examination of the phase diagram of these novel alloy systems. The revised phase diagram showed that the superconducting phase is stabilized by neighboring on the antiferromagnetic insulating phase. In addition we have examined the resistivity behavior under magnetic field and found that constant resistivity state at $x = 0.37\text{--}0.42$.

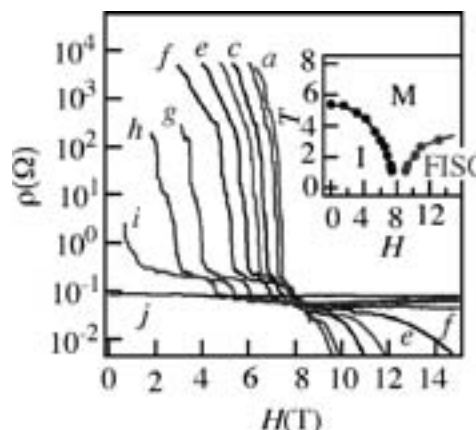


Figure 1. An example of T - H phase diagram of $\lambda\text{-(BETS)}_2\text{Fe}_x\text{Ga}_{1-x}\text{Cl}_4$ ($x = 0.66$), where H is applied parallel to the ac conduction plane: $a = 1.1$ K, $b = 1.5$, $c = 2.1$, $d = 2.6$, $e = 3.1$, $f = 3.6$, $g = 4.45$, $h = 4.9$, $i = 5.3$, $j = 4.1$, $k = 7.7$. It is shown that the MI transition was suppressed around 8 T and the field-induced superconducting phase begins to appear.

IV-C-2 Magnetic Transitions of Single-Component Molecular Metal $[\text{Au}(\text{tmdt})_2]$ and Its Alloy Systems

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[Ni(tmdt)₂] (tmdt = trimethylenetetrafulvalenedithiolate) is the first single-component molecular metal, where the metal electrons can be automatically generated by self-assembly of single kind of molecules. Though [Au(tmdt)₂] is isostructural to [Ni(tmdt)₂], the electronic band structures is completely different from that of [Ni(tmdt)₂] because the neutral bis(dithiolato)gold complex has an odd number of total electrons. Although it had been found that [Au(tmdt)₂] undergoes a possible antiferromagnetic transition around 100 K, more detail examination was needed. We have recently succeeded to obtain high-quality sample and performed the single crystal structure determination, resistivity measurements (on compacted pellet sample) and magnetic susceptibility. As shown in Figure 1, the temperature and field dependences of the susceptibility showed antiferromagnetic transition at 110 K. Recent electrical resistivity measurements using interdigitated electrodes by Tanaka et al. confirmed that the crystal retains metallic state even below 100 K. Thus, [Au(tmdt)₂] is clarified to be the first antiferromagnetic molecular metal with magnetic transition temperature at 110 K. The metallic state below the antiferromagnetic transition temperature is consistent with the band structure calculation suggesting the possibility of the partial nesting of the Fermi surfaces.

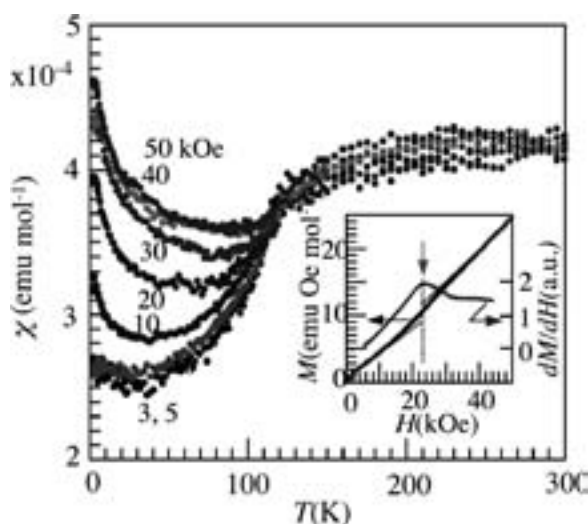


Figure 1. Temperature and magnetic field dependences of the susceptibilities of crystalline powder sample of [Au(tmdt)₂]. The inset is the *H*-dependences of *M* and *dM/dH* at 40 K. The gray arrow indicates the spin flop field

IV-C-3 Molecular Design and Physical Properties of Single-Component Molecular Metals

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The design of metallic crystals consisting of single-component molecules (*single-component molecular metal*) is explained on the basis of the examinations of frontier molecular orbitals and the simple extended-

Hückel tight-binding band pictures. To meet the conditions required to realize automatic carrier generation by self-assembly of the same kind of neutral molecules, a crystal of a transition metal complex molecule [Ni(tmdt)₂] with extended-TTF-type (TTF = tetrathiafulvalene) dithiolate ligands was synthesized, which was found to be the first single-component molecular metal. The X-ray structure analyses of the crystals of [(C₄H₉)₄N]₂[Ni(tmdt)₂] and neutral [Ni(tmdt)₂] provided information on the symmetry of the frontier molecular orbitals (the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)) from which the metallic bands are formed. The infrared and visible spectra of a crystalline powder sample of [Ni(tmdt)₂] showed a broad electronic absorption maximum at around 2200 cm⁻¹, suggesting an extremely small HOMO-LUMO gap. The physical properties of some of the hitherto-developed single-component molecular conductors are also briefly described.

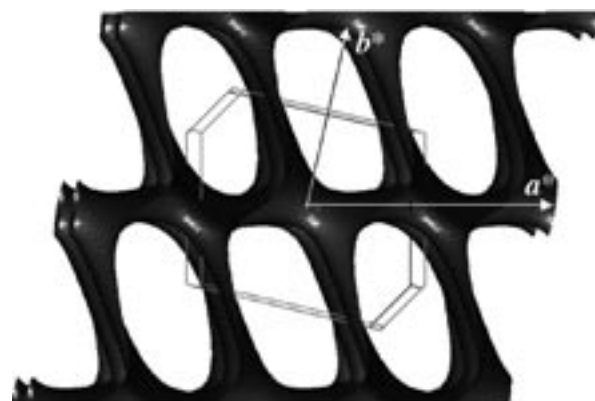


Figure 1. Fermi surfaces of single-component magnetic molecular metal, [Au(tmdt)₂] viewed along the *c** direction.

IV-C-4 A Molecular Conductor Based on Monoanionic Nickel Complex with Extended-TTF Type Ligands, (nBu₄N)[Ni(dmstfdt)₂] Exhibiting Weakly Metallic Behavior at High Temperature and Weak Ferromagnetism at Low Temperature

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A 1:1 tetrabutylammonium nickel complex with TTF-type ligands, (nBu₄N)[Ni(dmstfdt)₂] (dmstfdt = dimethyldiselenadithiafulvalenedithiolate) (**1**) is a unique molecular system with ambivalent character which exhibits weakly metallic behavior above room temperature and a weak ferromagnetism of localized electrons at low temperature. The X-ray structure analysis of **1** revealed that there are crystallographically independent two [Ni(dmstfdt)₂]⁻ anions (A and B) and two nBu₄N⁺ cations in the unit cell. The anions are arranged in a zigzag -ABA'B'- manner along the molecular side-by-side direction with a dihedral angle of molecular planes being 42.6°. The tight-binding band structure calculation

based on the extended Hückel approximation of **1** gave small three-dimensional electron and hole Fermi surfaces, which were compatible with the observed weakly metallic behavior around room temperature despite of the 1:1 stoichiometry of the complex. The χT values of **1** increased linearly from 0.129 to 0.383 emu·K·mol⁻¹ with decreasing temperature at 160–340 K, suggesting the gradual electron localization with lowering temperature. At 147 K, the complex **1** showed a sharp insulating transition associated with the localization of one electron on each nickel complex below 160 K. At 80–150 K, χ was well fitted by the Curie-Weiss law: $\chi = C/(T-\theta)$; $C = 0.383$ emu·K·mol⁻¹ and $\theta = -4$ K. A weak ferromagnetism was observed below 7 K. The coercive force was ± 1.5 kOe at 2.0 K.

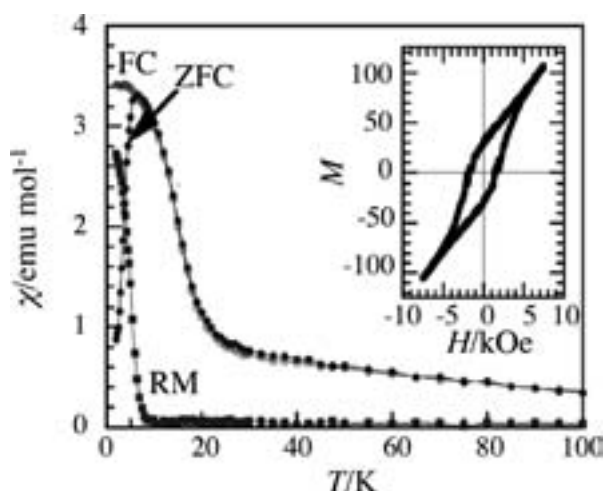


Figure 1. The zero-field-cooled (ZFC) and field-cooled (FC) susceptibilities and remnant magnetization (RM) as a function of temperature at 1 kOe for the polycrystalline sample of **1**. The insets shows the field dependence of the magnetization at 2.0 K.

IV-C-5 Ferroelectric Porous Molecular Crystal, [Mn₃(HCOO)₆](C₂H₅OH)

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Weak interaction is the most characteristic feature in the assembling of molecules. A typical example is the host-guest interaction in the porous materials, which have recently attracted large attention because of the high potentiality in the design of new materials with novel functions. Since the polar guest molecules form small assemblies loosely confined in the porous space, the porous material will be easily converted to the highly polarizable system by inserting polar guest molecules. If the polarized guest molecules are three-dimensionally ordered, a ferro- (or antiferro-) electric state will be realized. Furthermore, if we can combine the ferroelectrically polarizable guest molecules and the host porous lattice exhibiting magnetic order, we can obtain new type of “*multiferroic* molecular materials” where ferroelectricity and ferromagnetism coexist. We have recently discovered the first example of porous molecu-

lar crystal [Mn₃(HCOO)₆](C₂H₅OH) exhibiting ferroelectric transition at 165 K and ferrimagnetic transition at 8.5 K. The temperature dependence of the dielectric constants indicated that the ferroelectric transition is the first order transition. The dielectric measurements on the crystal with deuterated ethanol showed no significant change of T_c , suggesting that H-bond is not play an important role.

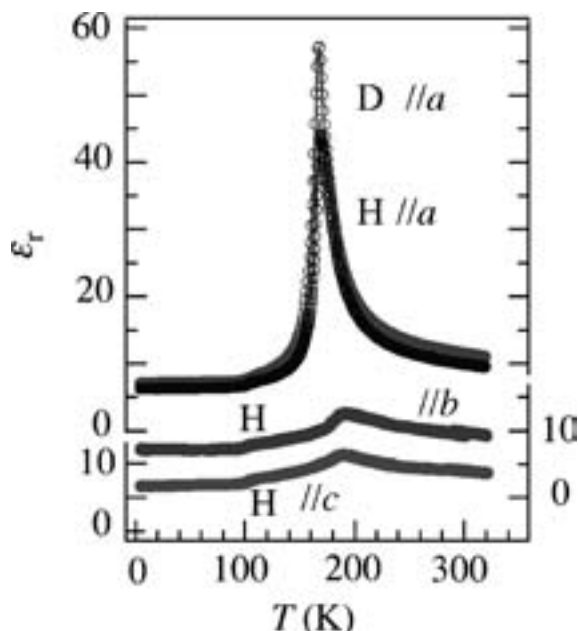


Figure 1. Dielectric constants (ϵ_r) of [Mn(HCOO)₆](C₂H₅OH) for the field $E//a$, b and c . The ϵ_r ($E//a$) of the crystal with deuterated ethanol, [Mn(HCOO)₆](C₂H₅OD) is also presented (open circles). D and H represent the dielectric constants of [Mn(HCOO)₆](C₂H₅OH) and [Mn(HCOO)₆](C₂H₅OD), respectively.

IV-C-6 Antiferroelect Porous Molecular Crystal with Guest Water Molecules

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We have recently found that a porous molecular crystal containing guest H₂O molecules, [Cu₃La₂(imino diacetate)₃](H₂O)₈ exhibits anomalously large dielectric constants and antiferroelectric hysteresis above the room temperature. At first, we measured the dielectric constants of the crystalline powder sample. But it gave anomalously large dielectric constant. In addition, the dielectric constant increased with increasing temperature around the room temperature. Similar behaviors were observed in various powdered crystals including famous ferroelectric material such as KH₂PO₄, which of course gave normal results when the single crystal was used. Therefore the measurement using the single crystal is essential for the dielectric experiments. In the present studies, the crystal with the size of 1.4 × 1.1 × 0.55 mm³ was used. As shown in Figure 1, ϵ_r showed a characteristic temperature dependence above 150 K. Though ϵ_r of [Cu₃La₂(iminodiacetate)₃](H₂O)₈ increased above 250

K, its temperature dependence became sluggish above 340 K. It was quite surprising that the antiferroelectric hysteresis loop was observed around 350 K where the guest H₂O molecules began to escape fairly rapidly. The dielectric properties of [Cu₃La₂(iminodiacetate)₆](D₂O)₈ were also examined.

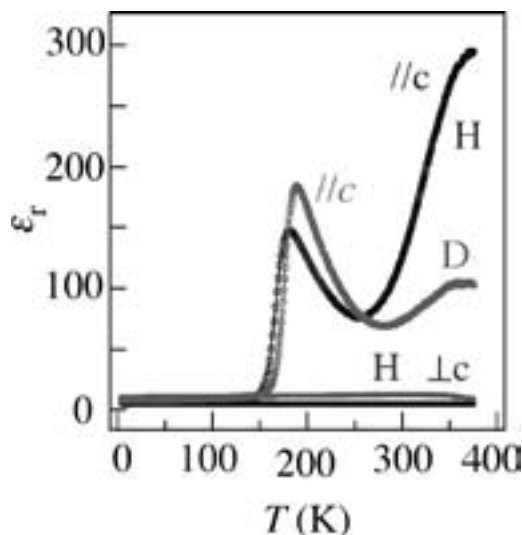


Figure 1. The dielectric constants ϵ_r of [Cu₃La₂(iminodiacetate)₆](H₂O)₈ for $E//c$ (black) and $E\perp c$ (gray). The black lines indicate ϵ_r of the guest-free crystal [Cu₃La₂(iminodiacetate)₆]. The dielectric constant of [Cu₃La₂(iminodiacetate)₆](D₂O)₈ is also presented ($E//c$ (gray)).

IV-C-7 High-Pressure Four-Probe Resistivity Measurements of Organic Crystals

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It is well known that resistivity measurements at extremely high pressure using diamond anvil revealed the superconductivities of various molecular materials such as hexa-iodobenzene and even O₂ which are usually considered to have no connection with electron conduction phenomena. Although the diamond anvil technique is very attractive one, its application to the four-probe resistivity measurements of the fragile organic crystals seems to contain many difficulties. Non-hydrostatic nature of the pressure medium at high pressure and anisotropic nature of molecular crystals will prevent the accurate resistivity measurements. However, the largest difficulty will exist in the method to connect four electrical leads (usually very thin gold wires) bonded to small sample crystal set in the small sample space in the diamond anvil cell with four lead terminals outside the diamond anvil. Several years ago, we have reported the superconductivity of (TMTTF)₂PF₆ discovered around 5 GPa by four-probe diamond anvil resistivity measurements and the improved method of the diamond anvil resistivity measurements. Very recently we have re-tried to perform high-pressure resistivity measurements of organic crystals by adopting the same method and found this method to be applicable at least up to 20 GPa.

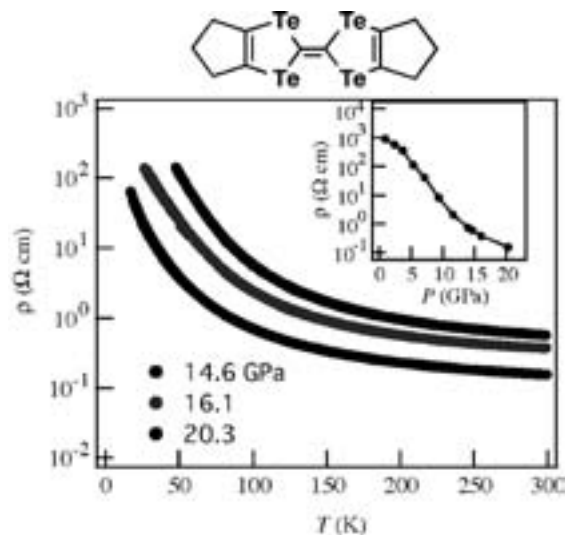


Figure 1. An example of the temperature dependence of the resistivity of molecular crystal up to 20 GPa. It should be noted that the room-temperature resistivity of the crystal of HMTTeF was reduced to about 0.15 Ωcm at 20 GPa.

IV-C-8 Electrical Conductivity Modulation Coupled to a High-Spin–Low-Spin Conversion in the Molecular System [Fe^{III}(qsal)₂][Ni(dmit)₂]₃·CH₃CN·H₂O

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Recently considerable interest has been attracted to the development of novel multi-functional molecular conductors. We have attempted to explore the possibility of reversible control of electrical conducting states by external stimuli. It is well known that the conducting properties of molecular conductors are changed greatly by the small modification of their crystal structures. Since the spin transition between the low-spin (LS) and the high-spin (HS) states accompanies a remarkable structural change in coordination bond length and geometry, the electrical conductivity of conducting spin-crossover (SCO) complex can be expected to be controlled by a structural change involving the spin conversion. The title complex was prepared by applying a constant voltage of [Fe(qsal)₂][Ni(dmit)₂]₂·2CH₃CN in acetonitrile [qsalH = *N*-(8-quinolyl)-salicylaldehyde, dmit = 4,5-dithiolato-1,3-dithiole-2-thione]. Ni(dmit)₂ molecules are arranged in a face-to-face manner to form a six-fold column along the *b* axis. These columns are arranged in a herring-bone type side-by-side to generate layers along the transverse direction. Fe(qsal)₂ cations are dimerized by π - π interactions. The Fe(qsal)₂ dimers construct a one-dimensional chain parallel to the Fe–Fe direction of a dimer, which is the *a*+*b* direction in the present case. Thus, Fe(qsal)₂ chains were interwoven with the Ni(dmit)₂ columns. Temperature dependence of magnetic moment and electrical resistivity of the 1:3 complex were shown in Figure 1. Interestingly, a hysteresis

esis loop of resistivity was observed in the temperature range of 90–120 K, which corresponds to the temperature range of the hysteresis of magnetic behavior. The relatively low resistivity in the heating process may be due to a sort of “chemical pressure effect” associated with the spin transition. Since the smaller size of SCO ions in the LS state than in the HS state will produce the more compact molecular packing of the cationic layers; this contraction exerts a pressure to the Ni(dmit)₂ conducting layers to make the system more conducting. Thus, to the best of our knowledge, this is the first evidence of a resistivity anomaly coupled with a spin transition in the SCO-molecular conductor hybrid.

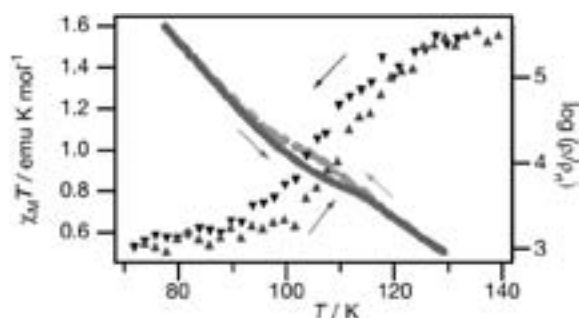


Figure 1. $\chi_M T$ vs. T plot (triangle, scale: left) and $\log(\rho/\rho_{RT})$ vs. T plot (circle, scale: right) of the 1:3 complex at the temperature range between 70 and 140 K.

IV-C-9 Structural Modifications Accompanying a Reproducible Spin-Crossover Phenomenon in [Fe(qsal)₂][Ni(dmise)₂] \cdot 2CH₃CN

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Recently we have developed novel Fe(III) spin-crossover (SCO) systems containing the Ni(dmit)₂ components: [Fe(qsal)₂][Ni(dmit)₂] \cdot 2CH₃CN showed a cooperative spin transition and a light-induced excited spin state trapping (LIESST) effect and [Fe(qsal)₂][Ni(dmit)₂] \cdot 3 \cdot CH₃CN \cdot H₂O demonstrated a conducting modulation coupled to a spin transition [qsalH = *N*-(8-quinoly)-salicylaldehyde, dmit = 4,5-dithiolato-1,3-dithiole-2-thione]. In particular, the synergic behavior between conducting and magnetic properties probably results from a sort of “chemical pressure effect” involving a spin conversion. However, it has never been successful to determine the crystal structures before and after the spin transition in both complexes. In the course of further studies to investigate more conducting systems in the related complexes, a reproducible spin transition with a small hysteresis loop that didn’t change by repeating the cooling and heating treatments was found in [Fe(qsal)₂][Ni(dmise)₂] \cdot 2CH₃CN [dmise is 4,5-dithiolato-1,3-dithiole-2-selone] (Figure 1). The crystal structure in the high temperature (HT) phase was isostructural to that of [Fe(qsal)₂][Ni(dmit)₂] \cdot 2CH₃CN at room temperature. The crystal system and symmetry does not change in the low temperature (LT) phase. Fe(qsal)₂ molecules formed one-dimensional chains through strong π – π interactions along the *b* axis and each chain was over-

lapped each other, to construct Fe(III) cation two-dimensional layers. The coordination bond lengths around the Fe atom indicated that the Fe(III) complex in the HT phase was almost in the high spin state and that in the LT phase was almost in the low spin state, respectively. These observations are consistent with the $\chi_M T$ values calculated from the SQUID data. A significant contraction in Fe(qsal)₂ two-dimensional layer was observed from the HT to the LT phases, suggesting this contraction would apply pressure to Ni(dmit)₂ layers.

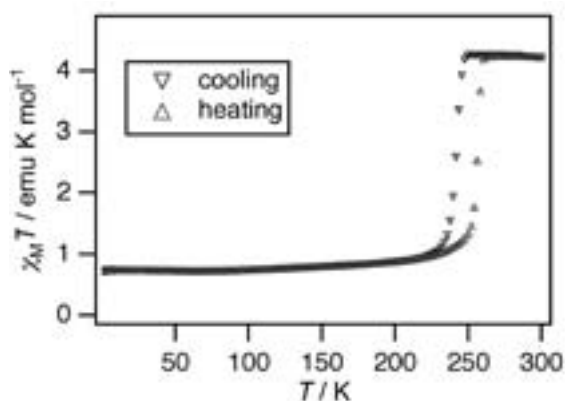


Figure 1. $\chi_M T$ vs. T plot of [Fe(qsal)₂][Ni(dmise)₂] \cdot 2CH₃CN.

IV-C-10 A Magnetic Organic Conductor Based on a π Donor with a Stable Radical and a Magnetic Anion—A Step to Magnetic Organic Metals with Two Kinds of Localized Spin Systems

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The synergetic action of magnetism and conductivity in the magnetic organic conductor consisting of π donor molecules and magnetic anions has recently attracted a considerable attention. On the other hand, there remains the long-standing target, that is, the magnetic organic conductor based on π donors having a stable organic radical part in the development of magnetic organic conductors. We have utilized a stable radical donor, TTP-PROXYL, which is 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (TTP) incorporating the 2,2,5,5-tetramethyl-1-pyrrolidin-1-ylloxyl (PROXYL) radical, and have obtained two isostructural conducting salts, (TTP-PROXYL)FeCl₄ and (TTP-PROXYL)GaCl₄. (TTP-PROXYL)FeCl₄ is a semiconductor with two kinds of localized spin systems which are organic radical spins and 3d spins of magnetic FeCl₄[−] ions, respectively. Compared with the isostructural GaCl₄ salt showing similar conducting properties, the π spin of the TTP-PROXYL radical cation disappears due to dimerization but the χT -value in FeCl₄ salt is 4.65 K emu mol^{−1}, indicating the coexistence of high-spin Fe³⁺ ($S = 5/2$) and PROXYL radical ($S = 1/2$). This observation will open a way to realize a new type of the magnetic organic conductors such as ferrimagnetic organic conductors.

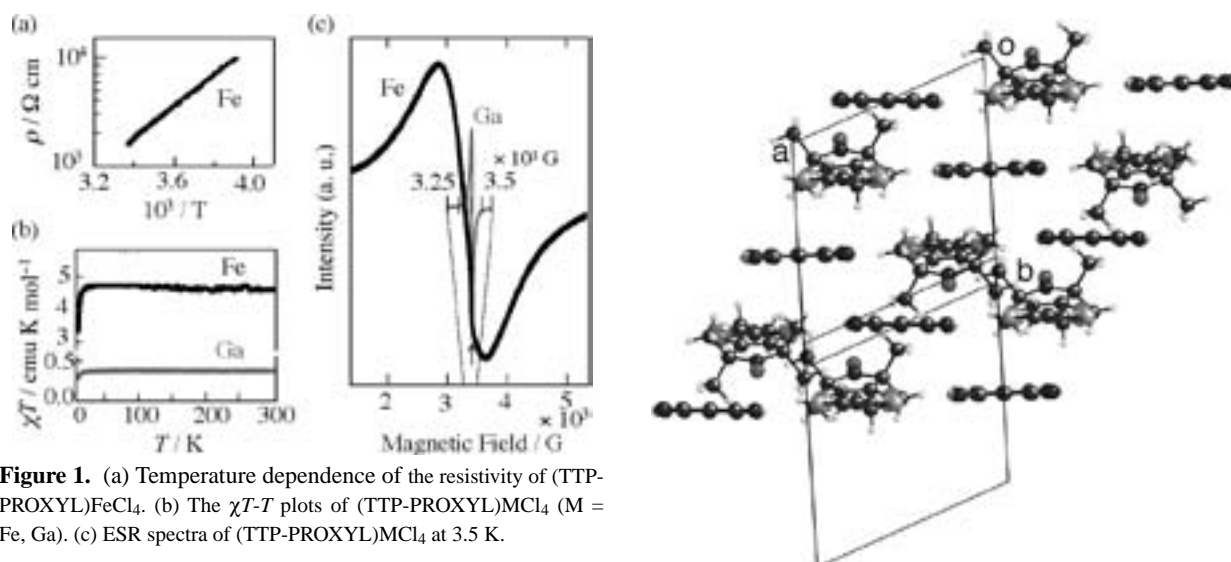


Figure 1. (a) Temperature dependence of the resistivity of (TTP-PROXYL)FeCl₄. (b) The χT - T plots of (TTP-PROXYL)MCl₄ (M = Fe, Ga). (c) ESR spectra of (TTP-PROXYL)MCl₄ at 3.5 K.

IV-C-11 Synthesis and Characterization of Novel PROXYL-Fused π -Electron Donors

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The development of novel magnetic molecular conductors based on the interplay between conducting electrons and localized spins has aroused a great attention in molecular materials science. To realize the coupling between conducting π -electrons and the spins on the stable organic radical in purely organic systems is one of the targets in this field. Despite several reports of syntheses and physical properties of π -electron donor or acceptor molecules with stable organic radicals and their conducting complexes, the number of well-characterized conducting complexes based on these donor or acceptor molecules is rare. Probably since the organic stable radicals are usually bulky and flexible, it is difficult to construct the conduction path based on the overlap between π -donors or acceptors and to give conducting crystals of good quality. In order to decrease a steric hindrance of a stable organic radical and to make a molecular structure rigid, we have designed and synthesized novel PROXYL radical-fused diselenadithiafulvalene (STF) derivatives. All the spectral data of new radical donors were in a good agreement with their molecular structures. Cyclic voltammograms revealed that the first and second one-electron oxidations occurred on the STF moieties, suggesting the possibility to generate cation biradical species. PROXYL-ET-STF afforded the 1:1 charge transfer complex with TCNQF₄. The radical donors (D) and acceptors (A) were alternately stacked to form irregular one-dimensional columns consisted of D-A-D trimers and A monomers (Figure 1). Bond length differences indicated that the complete charge transfer from the donor to the acceptor would occur. The magnetic data suggested that π -spins on the donor and acceptor were strongly antiferromagnetically coupled. The existence of NO radical spins was also suggested.

Figure 1. Crystal structure of (PROXYL-ET-STF)(TCNQF₄)·PhCl.